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(71) Applicant *(for all designated States except US)*: NIHON NOHYAKU CO., LTD. [JP/JP]; 2-5, Nihonbashi 1-chome, Chuo-ku, Tokyo 103 (JP).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: YAMAMOTO, Naoya [JP/JP]; 4-6, Onohara 1-chome, Kamisumachi, Kashima-gun, Ibaraki 314-01 (JP). UMIMOTO, Koji [JP/JP]; 5-6, Hondacho, Kawachinagano-shi, Osaka 586 (JP). NISHIGUCHI, Tsutomu [JP/JP]; 1-28, Nishinoyamacho, Kawachinagano-shi, Osaka 586 (JP). BABA, Koji [JP/JP]; 1-28, Nishinoyamacho, Kawachinagano-shi, Osaka 586 (JP). TABUCHI, Tatsuo [JP/JP]; 357, Taie, Hidakacho, Hidaka-gun, Wakayama 649-12 (JP). YOSHIDA, Masanori [JP/JP]; 5-3, Koyodai 2-chome, Hashimoto-shi, Wakayama 648 (JP).

(74) Agents: ASAMURA, Kiyoshi et al.; New Ohtemachi Building, Room 331, 2-1, Othemachi 2-chome, Chiyoda-ku, Tokyo 100 (JP).

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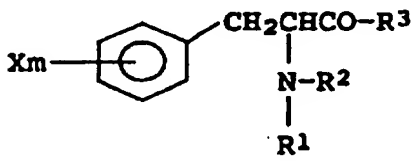
(54) Title: PHENYLALANINE DERIVATIVES, OPTICALLY ACTIVE SUBSTANCES, SALTS OR COORDINATION COMPOUNDS THEREOF, AND THEIR USE AS FUNGICIDES

(57) Abstract

The present invention provides a phenylalanine derivative represented by general formula (I), [wherein $R^1$ is H or an alkyl group, $R^2$ is H, an alkyl group, an alkoxycarbonyl group, a phenylalkyl group or the like, $R^1$ and $R^2$ being able to be taken together to represent an alkylene group which may contain O or N between adjacent carbon atoms of the carbon chain, or a phthaloyl group, $R^3$ is $OR^4$, $N(R^5)$-$R^6$ or $NHCH(R^7)(CH_2)nCOOR^8$ ($R^4$, $R^5$, $R^6$, $R^7$ and $R^8$ are as defined in the specification], a salt thereof, their optically active substances or coordination compounds, and a novel fungicide for fruit gardening containing any of them as an active ingredient.

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DESCRIPTION

# PHENYLALANINE DERIVATIVES, OPTICALLY ACTIVE SUBSTANCES, SALTS OR COORDINATION COMPOUNDS THEREOF, AND THEIR USE AS FUNGICIDES

## FIELD OF THE INVENTION

The present invention relates to phenylalanine derivatives, salts thereof, their optically active substances or coordination compounds, fungicides for fruit gardening containing any of these compounds as an active ingredient, and a method for application of the fungicides.

## BACKGROUND ART

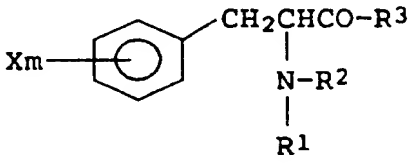
JP-A-49-109536 describes phenylalanine derivatives as effective in controlling rice blast and sheath blight but does not describe their effect against diseases in fruit gardening.

## SUMMARY OF THE INVENTION

Apple alternaria leaf spot and scab, pear black spot, etc. are typical diseases to be controlled in fruit growing. The present invention provides novel fungicides for fruit gardening used for controlling these diseases in fruit growing.

DISCLOSURE OF THE INVENTION

The present invention relates to fungicides for fruit gardening containing as an active ingredient any of phenylalanine derivatives represented by the following general formula (I), salts thereof, and their optically active substances or coordination compounds:




(I)

[wherein $R^1$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^2$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a ($C_1$-$C_6$)-alkoxycarbonyl group; an unsubstituted ($C_1$-$C_6$)alkyl-carbonyl group; a substituted ($C_1$-$C_6$)alkylcarbonyl group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl group; a substituted phenylcarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are

selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylsulfonyl group; a substituted phenylsulfonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group; or a substituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^1$ and $R^2$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, or a phthaloyl group, $R^3$ is a group represented by the formula:

$OR^4$

(wherein $R^4$ is a hydrogen atom; a ($C_1$-$C_{18}$)alkyl group; a halo($C_1$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; a cyclo($C_3$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group; a hydroxy($C_1$-$C_6$)-alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)-alkylthio($C_1$-$C_6$)alkyl group; a carboxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; a cyano($C_1$-$C_6$)alkyl group; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl

group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_2$-$C_6$)alkenyl group; a substituted phenyl($C_2$-$C_6$)alkenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylthio($C_1$-$C_6$)alkyl group; a substituted phenylthio($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl($C_1$-$C_6$)alkyl group; a substituted phenyl-

carbonyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom), a group represented by the formula:

$$N(R^5)\text{-}R^6$$

(wherein $R^5$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; an unsubstituted cyano($C_1$-$C_6$)alkyl group; a substituted cyano($C_1$-$C_6$)alkyl group having one or more substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups and phenyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy-($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; an unsubstituted

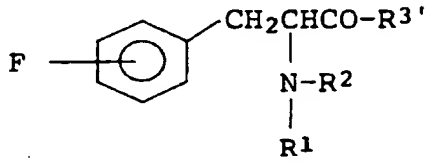
phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyloxy group; a substituted phenyl($C_1$-$C_6$)alkyloxy group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms,

nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; or a guanidyl($C_1$-$C_6$)alkyl group, and $R^6$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group or a ($C_2$-$C_6$)alkenyl group, $R^5$ and $R^6$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, and said ($C_1$-$C_6$)alkylene group being able to form a ring and have on the ring one or more substituents which may be the same or different and are selected from the group consisting of ($C_1$-$C_6$)alkyl groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, phenyl group, phenyl-($C_1$-$C_6$)alkyloxycarbonyl groups and phenyl($C_1$-$C_6$)alkyloxy groups) or a group represented by the formula:

$$NHCH(R^7)(CH_2)_nCOOR^8$$

(wherein $R^7$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, a cyclo($C_3$-$C_8$)alkyl group, a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group, a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group, a hydroxy-($C_1$-$C_6$)alkyl group, an amino($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms,

nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^8$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, and n is 0 or 1), X is a halogen atom, a nitro group, a cyano group, a hydroxyl group, an amino group, a ($C_1$-$C_6$)alkyl group, a halo($C_1$-$C_6$)alkyl group or a ($C_1$-$C_6$)alkoxy group, and m is an integer of 1 or 2], a method for application of the fungicides for fruit gardening, and novel compounds included in the compounds of the general formula (I) and not known in any literature, phenylalanine derivatives represented by the general formula (Ia):

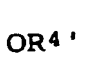



(Ia)

[wherein $R^1$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^2$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a ($C_1$-$C_6$)-

alkoxycarbonyl group; an unsubstituted ($C_1$-$C_6$)alkylcarbonyl group; a substituted ($C_1$-$C_6$)alkylcarbonyl group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl group; a substituted phenylcarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylsulfonyl group; a substituted phenylsulfonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl

group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group; or a substituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^1$ and $R^2$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, or a phthaloyl group, and $R^{3'}$ is a group represented by the formula:



(wherein $R^{4'}$ is a hydrogen atom, a ($C_3$-$C_{18}$)alkyl group; a halo($C_1$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; a cyclo($C_3$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group; a hydroxy($C_1$-$C_6$)-alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)-alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)-alkylthio($C_1$-$C_6$)alkyl group; a carboxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which

may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; a cyano($C_1$-$C_6$)alkyl group; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_2$-$C_6$)alkenyl group; a substituted phenyl($C_2$-$C_6$)alkenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on

the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylthio-($C_1$-$C_6$)alkyl group; a substituted phenylthio($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl($C_1$-$C_6$)alkyl group; a substituted phenyl-carbonyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom, provided

that when each of $R^1$ and $R^2$ is a hydrogen atom, $R^{4'}$ is other than hydrogen atom, tert-butyl group and benzyl group), a group represented by the formula:

$$N(R^5)-R^6$$

(wherein $R^5$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; an unsubstituted cyano($C_1$-$C_6$)alkyl group; a substituted cyano($C_1$-$C_6$)alkyl group having one or more substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups and phenyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)-alkoxy($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)-alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which

may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxy group; a substituted phenyl($C_1$-$C_6$)alkyloxy group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; or a guanidyl-($C_1$-$C_6$)alkyl group, and $R^6$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group or a ($C_2$-$C_6$)alkenyl group, $R^5$ and $R^6$ being able to be taken together to represent a ($C_1$-$C_6$)-alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the

carbon chain, and said ($C_1$-$C_6$)alkylene group being able to form a ring and have on the ring one or more substituents which may be the same or different and are selected from the group consisting of ($C_1$-$C_6$)alkyl groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, phenyl group, phenyl($C_1$-$C_6$)alkyloxycarbonyl groups and phenyl($C_1$-$C_6$)alkyloxy groups, provided that $R^1$, $R^2$, $R^5$ and $R^6$ are not hydrogen atoms at the same time, and that when $R^1$ is a tert-butoxycarbonyl group and $R^5$ is a benzyl group, $R^6$ is other than methyl group) or a group represented by the formula:

$$NHCH(R^7)(CH_2)_nCOOR^8$$

(wherein $R^7$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, a cyclo($C_3$-$C_8$)alkyl group, a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group, a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group, a hydroxy-($C_1$-$C_6$)alkyl group, an amino($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^8$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl

group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, and n is 0 or 1, provided that when each of $R^1$ and $R^2$ is a hydrogen atom, $R^7$ is other than methyl group and isobutyl group, and that when $R^1$ is a benzyloxycarbonyl group, $R^7$ is a hydrogen atom and n is 0, $R^8$ is other than ethyl group)], salts thereof, and optically active substances or coordination compounds of the phenylalanine derivatives or salts.

In the present specification, the term "($C_1$-$C_{18}$)alkyl group" means a linear or branched alkyl group of 1 to 18 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl, 1-methylbutyl, 2-methylbutyl, 1,2-dimethylpropyl, n-hexyl, isohexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 2,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl or the like. The term "halo($C_1$-$C_6$)alkyl group" means a substituted alkyl group of 1 to 6 carbon

atoms having as the substituent(s) one or more halogen atoms including fluorine atom, chlorine atom, bromine atom and iodine atom which may be the same or different, for example, trifluoromethyl or tetrafluoroethyl. The cyclo($C_3$-$C_6$)alkyl group includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, etc. The ($C_2$-$C_6$)alkenyl group includes alkenyl groups of 2 to 6 carbon atoms, such as vinyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 4-butenyl, etc. The alkynyl group includes alkynyl groups of 2 to 6 carbon atoms, such as ethenyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, etc. The hydroxy($C_1$-$C_6$)alkyl group includes hydroxymethyl, hydroxyethyl, etc. The ($C_1$-$C_6$)alkoxy-($C_1$-$C_6$)alkyl group includes methoxymethyl, ethoxymethyl, etc. The ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group includes methoxymethoxymethyl, ethoxymethoxymethyl, etc. The ($C_1$-$C_6$)alkylthio($C_1$-$C_6$)alkyl group includes methylthiomethyl, ethylthiomethyl, etc. The carboxy($C_1$-$C_6$)-alkyl group includes carboxymethyl, carboxyethyl, etc. The ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group includes methoxycarbonylmethyl, ethoxycarbonylmethyl, etc. The cyano($C_1$-$C_6$)alkyl group includes cyanomethyl, 1-cyano-1-methylethyl, etc. The substituted amino($C_1$-$C_6$)alkyl group having one or more substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups includes methylaminomethyl, methylaminoethyl, dimethylaminomethyl, dimethylaminoethyl, etc. The phenoxy($C_1$-$C_6$)alkyl group includes phenoxymethyl,

phenoxyethyl, etc. The phenyl($C_1$-$C_6$)alkyloxy($C_1$-$C_6$)-alkyl group includes, for example, substituted alkyl groups having a benzyloxy group, a phenethyloxy group or the like as the substituent. The phenylthio($C_1$-$C_6$)alkyl group includes phenylthiomethyl, phenylthioethyl, etc. The aromatic heterocyclic substituted ($C_1$-$C_6$)alkyl group includes pyridylmethyl, pyrimidylmethyl, thienylmethyl, furylethyl, etc. The phenyl($C_1$-$C_6$)alkyloxy group includes benzyloxy, phenethyloxy, etc. The ($C_1$-$C_6$)-alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain may form, for example, a pyrrolidino, piperidino, morpholino, thiomorpholino or piperazino group together with the nitrogen atom to which the ($C_1$-$C_6$)alkylene group is bonded, and the pyrrolidino, piperidino, morpholino, thiomorpholino or piperazino group may be substituted by a ($C_1$-$C_6$)alkyl group, a ($C_1$-$C_6$)alkoxycarbonyl group or a substituted or unsubstituted benzyl group.

When the phenylalanine derivative of the general formula (I) of the present invention is an amino acid, it has D-form and L-form. When the phenylalanine derivative is a dipeptide, it has diastereomers as stereoisomers. The phenylalanine derivative of the general formula (I) of the present invention includes mixtures of the above-mentioned optically active substances or diastereomers, and the individual optically active substances. The phenylalanine

derivative of the general formula (I) of the present invention may form a salt. As the salt, there can be usually exemplified salts with organic or inorganic bases or acids, for example, salts formed by addition of an acid such as hydrochloric acid, sulfuric acid, nitric acid, hydrobromic acid, phosphoric acid, perchloric acid, thiocyanic acid, boric acid, formic acid, acetic acid, haloacetic acid, propionic acid, glycolic acid, citric acid, tartaric acid, succinic acid, gluconic acid, lactic acid, malonic acid, fumaric acid, anthranilic acid, benzoic acid, cinnamic acid, p-toluenesulfonic acid, alkylbenzenesulfonic acid, naphthalenesulfonic acid, sulfanilic acid or the like; salts with organic bases such as amines; and salts with alkaline earth metal such as sodium, potassium, etc., or metals such as aluminum, etc. The phenylalanine derivative of the general formula (I) of the present invention may form also a metal coordination compound, for example, a coordination compound with zinc, nickel, cobalt, copper, iron or the like.

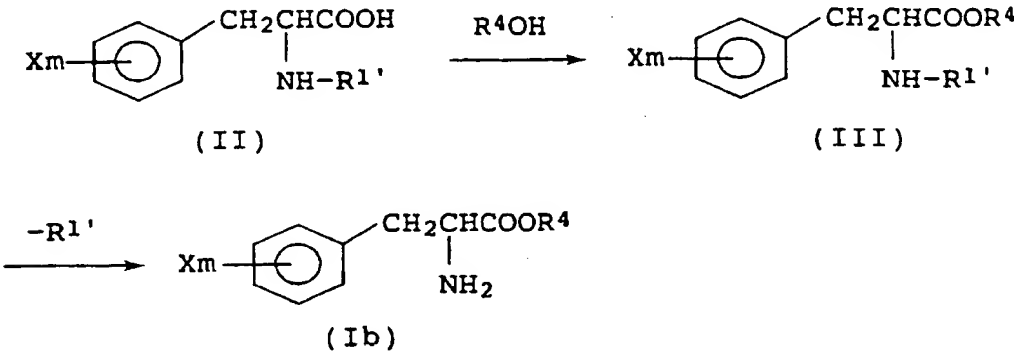
Preferable examples of the substituents of the phenylalanine derivative represented by the general formula (I) of the present invention are as follows: each of $R^1$ and $R^2$ is preferably a hydrogen atom or a $(C_1-C_6)$alkyl group, particularly preferably a hydrogen atom, $R^3$ is preferably $-OR^4$ wherein $R^4$ is preferably a hydrogen atom, a $(C_1-C_6)$alkyl group, a cyclo$(C_3-C_8)$-alkyl group, a phenyl$(C_1-C_6)$alkyl group or a

substituted phenyl($C_1$-$C_6$)alkyl group, particularly preferably a ($C_1$-$C_6$)alkyl group or a benzyl group, and X is preferably a halogen atom.

The phenylalanine derivative of the general formula (I) of the present invention can be produced, for example, by any of the processes illustrated below.

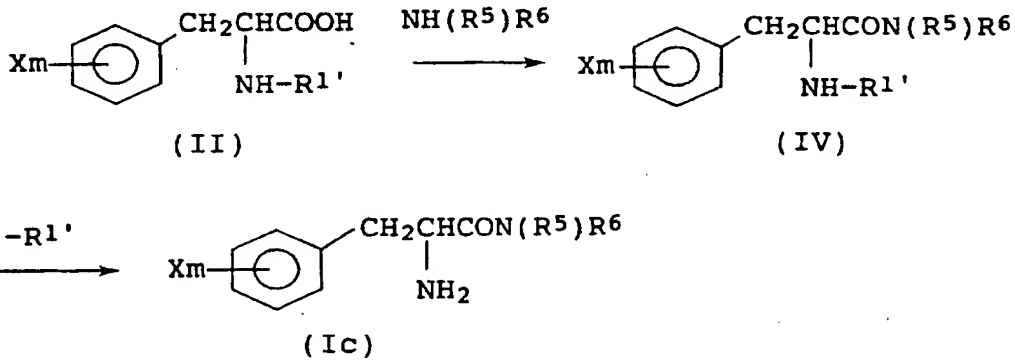
Scheme I

Process A



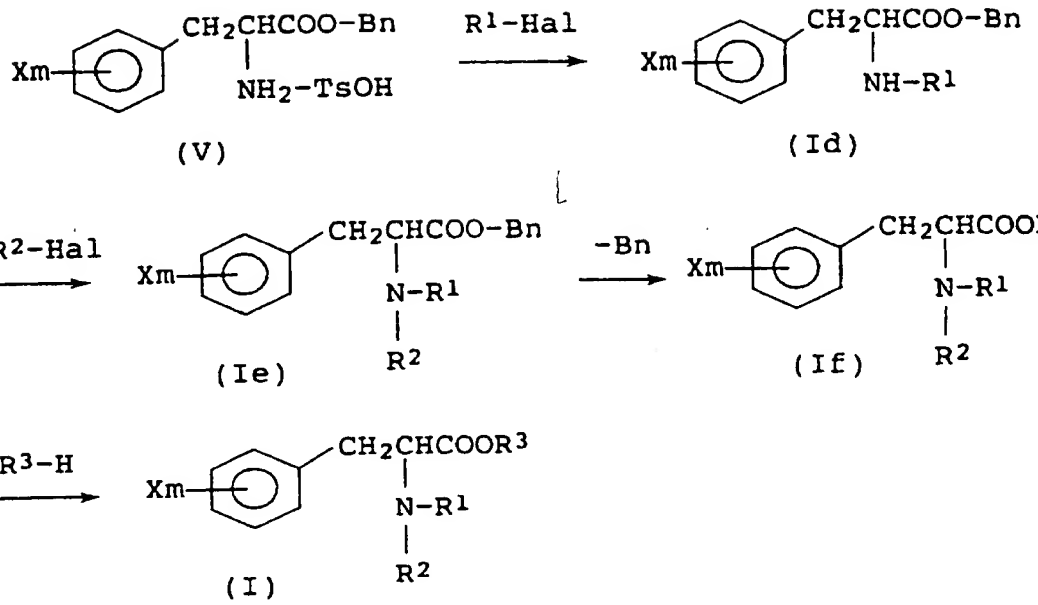

(II) (III) (Ib)

Process B




(II) (IV) (Ic)

Process C




(V) (Id) (Ie) (If) (I)

wherein $R^1$, $R^2$, $R^3$, $R^4$, $R^5$ and m are as defined above, $R^6$ is the same as $R^5$ or is $CH(R^7)(CH_2)_nCOOR^8$ (wherein $R^7$, $R^8$ and n are as defined above), $R^{1'}$ is a benzyloxycarbonyl group or a tert-butoxycarbonyl group, Bn is a benzyl group, TsOH is p-toluenesulfonic acid, and Hal is a halogen atom.

In this production process, examples of inert solvent suitable for each production step are water and all inert solvents which are not changed under the reaction conditions. Preferable examples of such inert solvents are alcohols (e.g. methanol, ethanol, n-propanol and isopropanol), ethers (e.g. diethyl ether, dioxane, diisopropyl ether, tetrahydrofuran, glycol monomethyl ether and glycol dimethyl ether), chlorinated hydrocarbons (e.g. chloroform and dichloromethane), amides (e.g. dimethylformamide, dimethylamine and

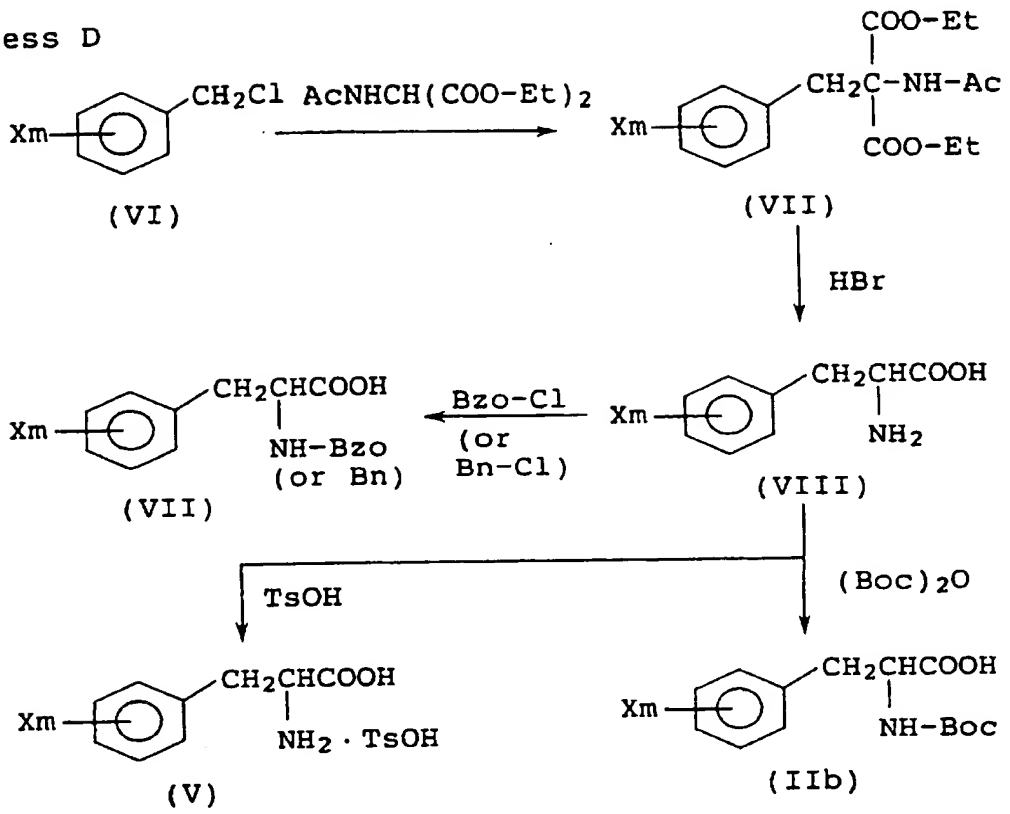
hexamethyl-phosphorylamide), glacial acetic acid, dimethyl sulfoxide, acetonitrile and pyridine. In each reaction, although one of the reactants may be used in excess, it is preferably used in an amount of 1 equivalent per equivalent of the other. The reaction temperature ranges from -20°C to the boiling point of the solvent. The reaction time may be chosen in the range of 0.5 hour to 24 hours.

Of the phenylalanine derivatives represented by the general formula (I), D,L-amino acids can be produced by a process based on the content of Journal of the Chemical Society, 1951, p.2071. p-Toluenesulfonic acid salt of the phenylalanine derivative can be produced by a process based on the content of "Fundamentals and Practice of Peptide Synthesis", p. 43, Maruzen Co., Ltd. Optically active substances of the phenylalanine derivative can be separated from their racemic modification by a high performance liquid chromatography according to a method described in Journal of Chromatography, Vol. 405, p. 145 (1887). Optically active substances also can be prepared through optical resolution method using optically active amines or acids as a optically resoluting agent.

The starting compound, i.e., the compound of the general formula (II) or (V) is a well-known substance and can be produced, for example, by the following conventional process described in Journal of the Chemical Society, 1951, p.2071.

Scheme II

Process D




wherein Bn and TsOH are as defined above, Et is an ethyl group, Ac is an acetyl group, Bzo is a benzyloxycarbonyl group, and Boc is a tert-butoxycarbonyl group.

The phenylalanine derivatives of the general formula (I) of the present invention are useful as agricultural fungicides and are excellent particularly as fungicides for fruit trees for controlling, for example, Alternaria leaf spot, scab and black spot.

For formulating the phenylalanine derivative of the general formula (I) of the present invention into an agricultural and horticultural fungicide, the phenylalanine derivative and optionally an adjuvant are

blended with a suitable inert carrier in a proper proportion and prepared into a suitable preparation form such as a solution, a suspension, an oil formulation, an emulsifiable concentrate, dust, granules, a wettable powder, tablets, pellets, a paste or an aerosol through dissolution, dispersion, suspension, mixing, impregnation, adsorption or sticking. As the inert carrier, any of solid, liquid and gaseous carriers may be used. As the solid carrier, there can be exemplified soybean flour, wood flour, bark flour, saw dust, powdered tobacco stalks, powdered walnut shells, bran, powdered cellulose, extraction residue of vegetables, powdered synthetic polymers or resins, clays (e.g. kaolin, bentonite, and acid clay), talcs (e.g. talc and pyrophyllite), silica powders or flakes (e.g. diatomaceous earth, silica sand, mica, synthetic silicates, and synthetic, high-dispersion silicic acid), activated carbon, powdered sulfur, powdered pumice, calcined diatomaceous earth, ground brick, fly ash, sand, calcium carbonate powder, calcium phosphate powder and other inorganic or mineral powders, chemical fertilizers (e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ammonium chloride and urea), and compost. These carriers may be used alone or as a mixture thereof.

The liquid carrier is that which itself has solubility or which is without such solubility but is capable of dispersing an active ingredient with the aid of an adjuvant. The following are examples of the

liquid carrier and can be used alone or as a mixture thereof. Water; alcohols such as methanol, isopropanol and ethylene glycol; ketones such as acetone and cyclohexanone; ethers such as ethyl ether, dioxane, tetrahydrofuran and Cellosolve; aliphatic hydrocarbons such as gasoline and kerosene; aromatic hydrocarbons such as benzene, toluene, solvent naphtha and methylnaphthalene; halogenated hydrocarbons such as dichloroethane and chloroform; esters such as ethyl acetate and diisopropyl phthalate; amides such as dimethylformamide and dimethylacetamide; nitriles such as acetonitrile; and dimethyl sulfoxide.

The gaseous carrier includes, for example, Freon, butane gas, dimethyl ether, carbonic acid gas and LPG (liquefied petroleum gas).

As the adjuvant, the following adjuvants can be exemplified. They are used depending upon purposes and used alone or in combination in some cases, or need not be used at all. To emulsify, disperse, dissolve and/or wet an active ingredient, there can be used surfactants such as polyoxyethylene alkylaryl ethers, polyoxyethylene alkyl ethers, polyoxyethylene higher fatty acid esters, polyoxyethylene resinates, polyoxyethylene sorbitan monooleate, alkylaryl sorbitan monolaurates, alkylbenzenesulfonates, alkylnaphthalenesulfonates, ligninsulfonates and higher alcohol sulfate esters.

Further, to stabilize the dispersion of an

active ingredient, tackify it and/or bind it, there may be used adjuvants such as casein, gelatin, starch, alginic acid, CMC, gum arabic, agar, polyvinyl alcohols, turpentine, bran oil, bentonite, lignin, and sulfite liquor.

To improve the flowability of a solid product, there may be used adjuvants such as waxes, stearic acid and alkyl phosphates.

Adjuvants such as naphthalenesulfonic acid condensation products and phosphates may be used as a peptizer for dispersible products.

Defoaming agents such as silicon oils may also be added.

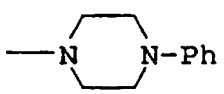
When the phenylalanine derivative of the general formula (I) of the present invention is applied as a fungicide for fruit gardening, the applying dosage of the active ingredient, i.e., the phenylalanine derivative is varied depending on various factors such as a purpose, a plant to be treated, a growth state of the plant, tendency of disease occurence, weather, environmental conditions, a preparation form, an application method, an application site and an application time. It is properly chosen in the range of 0.1 g to 1 kg per 10 ares.

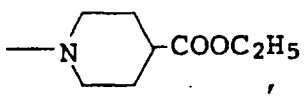
The content of the active ingredient may be varied as required. In dusts or granules, the content is usually 0.5 to 20%. In emulsifiable concentrates, suspensions or wettable powders, the content is 0.1 to

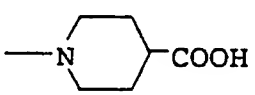
90%.

The fungicide for fruit gardening containing the compound of the present invention as an active ingredient may be used in admixture with other agricultural and horticultural fungicides in order to expand both spectrum of controllable diseases and the period of time when effective applications are possible or to reduce the dosage. The desired effect of the present inventive fungicide for fruit gardening containing the compound of the present invention as an active ingredient can be obtained by applying the fungicide at a season at which the diseases are expected to occur, before their occurrence or at the time when their occurrence is confirmed.

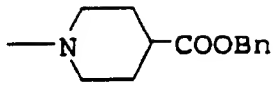
Typical examples of the phenylalanine derivative of the general formula (I) of the present invention are given in Table 1 but they are not intended in any way to limit the scope of the present invention. In Table 1, Et, Bn, Bzo, Boc and TsOH are as defined above, Me is a methyl group, i-Pr is an isopropyl group, i-Bu is an isobutyl group, t-Bu is a tert-butyl group, Ph is a phenyl group, Bz is a benzoyl group, and DSA is a dodecylbenzenesulfonic acid. $Q^1$ through $Q^7$ denote the following substituents:

$Q^1$:  ,

$Q^2$:  ,

$Q^3$:  ,

Q4:



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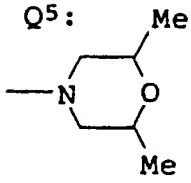
Q5:



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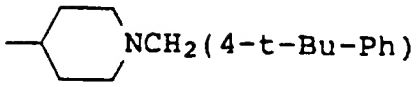
Q6:



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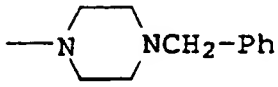
Q7:



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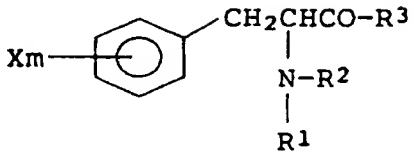
General formula (I):



(I)

Table 1

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 1 | 4-F | H | 4-$MePhSO_2$ | OH | m.p. 142-143°C |
| 2 | 4-F | H | (2,4,6(i-Pr)$_3$Ph)$SO_2$ | OH | m.p. 168-169°C |
| 3 | 4-F | H | 4-COOMePhCO | OH | m.p. 135-136°C |
| 4 | 4-F | H | 4-F-Bz | OH | m.p. 215-216°C |
| 5 | 4-F | H | H | NH-$CH_3$ | m.p. 115-117°C (acetate) |
| 6 | 4-F | H | H | NH-cyclohexyl | m.p. 115-116°C (acetate) |
| 7 | 4-F | H | H | NH-(2,4-$Cl_2$-Ph) | m.p. 228-230°C |
| 8 | 4-F | H | H | $Q^1$ | paste |
| 9 | 4-F | H | Boc | NH-Bn | m.p. 169-170°C |
| 10 | 4-F | H | H | NH-Bn | m.p. 67 - 68°C |
| 11 | 4-F | H | H | O-(4-F-Bn) | paste |
| 12 | 4-F | H | H | O-(4-t-Bu-Bn) | m.p. 56 - 57°C |
| 13 | 4-F | H | H | O-(4-$NO_2$-Bn) | paste |
| 14 | 4-F | H | H | O-t-Bu | paste |
| 15 | 4-F | H | H | O-i-$C_5H_{11}$ | paste |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 16 | 4-F | H | H | O-$CH_2CF_2CF_3$ | paste |
| 17 | 4-F | H | H | O-($F_5$-Bn) | paste |
| 18 | 4-F | H | Bzo | NH-$CH_3$ | m.p. 155-156°C |
| 19 | 4-F | H | Bzo | NH-cyclohexyl | m.p. 183-184°C |
| 20 | 4-F | H | 4-F-Bz | O-Bn | m.p. 142-143°C |
| 21 | 4-F | H | 2-COOH-Bz | O-Bn | m.p. 159-160°C |
| 22 | 4-F | H | Bzo | NH-(2,4-$Cl_2$-Ph) | m.p. 170-171°C |
| 23 | 4-F | H | 4-Me-$PhSO_2$ | O-Bn | m.p. 130-131°C |
| 24 | 4-F | H | 2,4,6(i-Pr)$_3$$PhSO_2$ | O-Bn | m.p. 134-135°C |
| 25 | 4-F | H | 4-COOMePhCO | O-Bn | mp. 168-169°C |
| 26 | 4-F | | COPhCO | O-Bn | m.p. 83 - 84°C |
| 27 | 4-F | H | 4-t-Bu-Bn | O-Bn | paste |
| 28 | 4-F | Me | 4-t-Bu-Bn | O-Bn | m.p. 40 - 41°C |
| 29 | 4-F | H | Bzo | O-t-Bu | paste |
| 30 | 4-F | H | Bzo | O-i-$C_5H_{11}$ | paste |
| 31 | 4-F | H | Bzo | O-$CH_2CF_2CF_3$ | m.p. 70 - 71°C |
| 32 | 4-F | H | Boc | O-$CH_2CH$=CH(4-F-Ph) | paste |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 33 | 4-F | H | Boc | O-$CH_2CH$=CH(4-$OCH_2CH_2CF_3$-Ph) | paste |
| 34 | 4-F | H | Boc | O-(4-MeO-Bn) | m.p. 150-151°C |
| 35 | 4-F | H | Boc | O-($F_5$-Bn) | m.p. 95 - 96°C |
| 36 | 4-F | H | Bzo | NH-$CH_2CH_2$COO-Bn | m.p. 136-137°C |
| 37 | 4-F | H | H | NH-$CH_2CH_2$COOH | m.p. 199-200°C |
| 38 | 4-F | H | Bzo | $Q^2$ | m.p. 87 - 88°C |
| 39 | 4-F | H | Bzo | $Q^1$ | m.p. 116-117°C |
| 40 | 4-F | H | Bzo | $Q^3$ | m.p. 180-181°C |
| 41 | 4-F | H | H | $Q^3$ | m.p. 235-237°C |
| 42 | 4-F | H | 4-F-Bz | NH-CH(i-Pr)COO-Bn | m.p. 155-158°C |
| 43 | 4-F | H | 4-F-Bz | NH-CH(i-Pr)COOH | m.p. 110-112°C |
| 44 | 4-F | H | Bzo | NH-CH(i-Pr)COO-Bn | m.p. 120-122°C |
| 45 | 4-F | H | H | NH-CH(i-Pr)COOH | m.p. 142-145°C |
| 46 | 4-F | H | H | $Q^2$ | m.p. 109-110°C (acetate) |
| 47 | 4-F | H | H | NH-CH(i-Pr)COO-Bn | paste |
| 48 | 4-F | H | Boc | NH-CH(4-F-Bn)COO-Bn | m.p. 129-130°C |



- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 49 | 4-F | H | H | NH-CH(4-F-Bn)COO-Bn | m.p. 74 - 75°C |
| 50 | 4-F | H | Boc | Q4 | paste |
| 51 | 4-F | H | H | Q4 | paste |
| 52 | 4-F | H | H | NH-CH(4-F-Bn)COOH | m.p. 255-265°C |
| 53 | 4-F | H | Boc | NH-$CH_2$COO-Bn | m.p. 90 - 95°C |
| 54 | 4-F | H | H | NH-$CH_2$COO-Bn | paste |
| 55 | 4-F | H | H | NH-CH(Bn)COO-Bn | m.p. 269-273°C (L-form) |
| 56 | 4-F | H | H | NH-CH(Bn)COO-Bn | m.p. 268-273°C (D-form) |
| 57 | 4-F | H | H | NH-CH(Bn)COOH | m.p. 148-150°C (L-form) |
| 58 | 4-F | H | Boc | NH-Ph | m.p. 188-189°C |
| 59 | 4-F | H | H | NH-Ph | m.p. 69 - 70°C |
| 60 | 4-F | H | Boc | NH-(4-t-Bu-Ph) | m.p. 172-173°C |
| 61 | 4-F | H | H | NH-(4-t-Bu-Ph) | m.p. 141-142°C |
| 62 | 4-F | H | Boc | NH-CH(Me)Ph | m.p. 174-175°C |
| 63 | 4-F | H | H | NH-CH(Me)Ph | $n_D$: 1.3000 (27°C) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 64 | 4-F | H | Boc | NH-$CH_2CH_2$Ph | m.p. 147-148°C |
| 65 | 4-F | H | H | NH-$CH_2CH_2$Ph | m.p. 52 - 53°C |
| 66 | 4-F | H | H | O-Bn | m.p. 96 - 98°C (DSA salt) |
| 67 | 4-F | H | H | O-$(CH_2)_4$Me | paste |
| 68 | 4-F | H | H | O-$(CH_2)_7$Me | paste |
| 69 | 4-F | H | H | O-cyclopentyl | paste |
| 70 | 4-F | H | H | O-$(CH_2)_2$(4-F-Bn) | paste |
| 71 | 4-F | H | H | O-$CH_2CH=CH_2$ | paste |
| 72 | 4-F | H | H | O-$CH_2C\equiv CH$ | paste |
| 73 | 4-F | H | H | O-$(CH_2)_2O(CH_2)_3$Me | paste |
| 74 | 4-F | H | H | O-$(CH_2)_2$S-t-Bu | paste |
| 75 | 4-F | H | H | O-$(CH_2)_2$S-Ph | paste |
| 76 | 4-F | H | Boc | O-$(CH_2)_7$Me | $n_D$: 1.3008 (27°C) |
| 77 | 4-F | H | Boc | O-cyclopentyl | m.p. 73 - 74°C |
| 78 | 4-F | H | Boc | O-$(CH_2)_2$(4-F-Ph) | $n_D$: 1.3141 (27°C) |
| 79 | 4-F | H | Boc | O-$CH_2CH=CH_2$ | $n_D$: 1.3010 (24°C) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 80 | 4-F | H | Boc | O-$CH_2C\equiv CH$ | m.p. 57 - 60°C |
| 81 | 4-F | H | Boc | O-$(CH_2)_2O(CH_2)_3Me$ | $n_D$: 1.3125 (27°C) |
| 82 | 4-F | H | Boc | O-$(CH_2)_2S$-t-Bu | $n_D$: 1.3114 (27°C) |
| 83 | 4-F | H | Boc | O-$(CH_2)_2S$-Ph | m.p. 47 - 49°C |
| 84 | 4-F | H | Boc | $N(i\text{-}Bu)_2$ | m.p. 108-109°C |
| 85 | 4-F | H | H | $N(i\text{-}Bu)_2$ | $n_D$: 1.4846 (26°C) |
| 86 | 4-F | H | Boc | N(Me)-cyclohexyl | $n_D$: 1.3000 (24°C) |
| 87 | 4-F | H | H | N(Me)-cyclohexyl | $n_D$: 1.5716 (24°C) |
| 88 | 4-F | H | Boc | $Q^5$ | m.p. 114-115°C |
| 89 | 4-F | H | H | $Q^5$ | $n_D$: 1.5178 (25°C) |
| 90 | 4-F | H | Boc | NH-(4-t-Bu-Bn) | m.p. 135-137°C |
| 91 | 4-F | H | H | NH-(4-t-Bu-Bn) | m.p. 78 - 80°C |
| 92 | 4-F | H | Boc | NH-$C(Me)_2$-Ph | m.p. 172-173°C |
| 93 | 4-F | H | H | NH-$C(Me)_2$-Ph | $n_D$: 1.5124 (25°C) |
| 94 | 4-F | H | Boc | NH(2,4-$Cl_2$-Bn) | m.p. 185-187°C |
| 95 | 4-F | H | H | NH(2,4-$Cl_2$-Bn) | m.p. 191-193°C |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 96 | 4-F | H | H | $NH-C(CH_3)(Pr\text{-}i)-CN$ | $n_D$: 1.5074 (24°C) |
| 97 | 4-F | H | H | $O-CH_2COOEt$ | paste |
| 98 | 4-F | H | H | $O-(CH_2)_2CN$ | paste |
| 99 | 4-F | H | H | $NH-CH_2C\equiv CH$ | m.p. 72 - 73°C |
| 100 | 4-F | H | H | NH-Bn | m.p. 84 - 85°C |
| 101 | 4-F | H | H | $NH-CH_2CH_2$(4-t-Bu-Ph) | m.p. 96 - 97°C |
| 102 | 4-F | H | MeCO | O-Bn | m.p. 90 - 91°C |
| 103 | 4-F | H | $ClCH_2CO$ | O-Bn | m.p. 59 - 60°C |
| 104 | 4-F | H | EtOCO | O-Bn | $n_D$: 1.5030 (23°C) |
| 105 | 4-F | H | H | O-(4-PhO-Bn) | m.p. 153-155°C (hydrochloride) |
| 106 | 4-F | H | H | O-(4-Ph-Bn) | m.p. 208-210°C (hydrochloride) |
| 107 | 4-F | H | H | $O-(CH_2)_{11}CH_3$ | paste (hydrochloride) |
| 108 | 4-F | H | H | O-Ph | m.p. 190-191°C (hydrochloride) |
| 109 | 4-F | H | H | NH-CH(i-Bu)COO-Bn | $n_D$: 1.4003 (22°C) (L-form) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 110 | 4-F | H | H | NH-CH(i-Bu)COOH | m.p. 225-230°C (L-form) |
| 111 | 4-F | H | H | $O-CH_2CH_2OCH_2CH_2OCH_3$ | m.p. 125-127°C (hydrochloride) |
| 112 | 4-F | H | H | $O-(CH_2)_5CH_3$ | paste (hydrochloride) |
| 113 | 4-F | H | H | $O-(CH_2)_6CH_3$ | paste (hydrochloride) |
| 114 | 4-F | H | H | $O-(CH_2)_8CH_3$ | m.p. 68 - 70°C (hydrochloride) |
| 115 | 4-F | H | H | $O-(CH_2)_{17}CH_3$ | m.p. 75 - 76°C (hydrochloride) |
| 116 | 4-F | H | H | $O-CH_2COOEt$ | m.p. 131-132°C (hydrochloride) |
| 117 | 4-F | H | H | $O-(CH_2)_2CN$ | m.p. 125-128°C (hydrochloride) |
| 118 | 4-F | H | H | $O-CH_2COPh$ | m.p. 184-185°C (hydrochloride) |
| 119 | 4-F | H | H | $O-CH(CH_2CH_2CH_3)_2$ | m.p. 95 - 97°C (hydrochloride) |
| 120 | 4-F | H | H | $O-CH(CH_3)-(CH_2)_6CH_3$ | m.p. 118-120°C (hydrochloride) |
| 121 | 4-F | H | H | $O-CH_2CH=CHCH_2CH_2CH_3$ | m.p. 125-126°C (hydrochloride) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 122 | 4-F | H | H | $O-CH_2CH=C(CH_3)_2$ | m.p. 139-141°C (hydrochloride) |
| 123 | 4-F | H | H | $O-CH(Ph)_2$ | m.p. 169-171°C (hydrochloride) |
| 124 | 4-F | H | H | O-cyclohexyl | m.p. 189-191°C (hydrochloride) |
| 125 | 4-F | H | H | O-cycloheptyl | m.p. 168-169°C (hydrochloride) |
| 126 | 4-F | H | H | O-cyclooctyl | m.p. 148-149°C (hydrochloride) |
| 127 | 4-F | H | H | $O-CH_2$-cyclohexyl | m.p. 171-172°C (hydrochloride) |
| 128 | 4-F | H | H | $O-CH(CH_3)-n-C_5H_{11}$ | m.p. 124-127°C (hydrochloride) |
| 129 | 4-F | H | H | $O-(CH_2)_2NMe_2$ | paste |
| 130 | 4-F | H | MeCO | $O-(CH_2)_8Me$ | $n_D$: 1.4852 (23°C) |
| 131 | 4-F | H | H | $Q^6$ | m.p. 244-247°C (dihydrochloride) |
| 132 | 4-F | H | H | $Q^7$ | m.p. 185-190°C (dihydrochloride) |
| 133 | 2-F | H | H | NH-CH(i-Bu)COO-Bn | m.p. 119-122°C (hydrochloride, L-form) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 134 | 4-F | H | H | NH-CH($CH_2$-cyclohexyl)COO-Bn | $n_D$: 1.5018 (23°C) (hydrochloride) |
| 135 | 4-F | H | H | NH-$(CH_2)_6CH_3$ | m.p. 151-152°C |
| 136 | 4-F | H | H | NH-$CH_2CH_2$(4-Me-Ph) | m.p. 78 - 80°C |
| 137 | 4-F | H | $CF_3CO$ | O-Bn | m.p. 137-140°C |
| 138 | 4-F | H | H | NH-CH($CH_2$-cyclohexyl)COO-Bn | m.p. 174-176°C (hydrochloride) |
| 139 | 4-F | H | H | NH-$CH_2CH_2$(4-n-Bu-Ph) | m.p. 61 - 62°C |
| 140 | 4-F | H | H | NH-$CH_2CH_2$(4-i-Pr-Ph) | m.p. 171-174°C (hydrochloride) |
| 141 | 4-F | H | H | NH-$CH_2CH_2$(2,4-$Me_2$-Ph) | m.p. 190-192°C (hydrochloride) |
| 142 | 4-F | H | H | NH-$CH_2CH_2$(3,4-$(MeO)_2$-Ph) | $n_D$: 1.5492 (20°C) |
| 143 | 4-F | H | H | O-n-octyl | m.p. 77 - 82°C (hydrochloride) |
| 144 | 4-F | H | t-BuCO | O-Bn | m.p. 81 - 83°C |
| 145 | 4-F | H | i-PrCO | O-Bn | m.p. 93 - 94°C |
| 146 | 4-F | H | n-Pr | O-Bn | m.p. 71 - 72°C |
| 147 | 4-F | H | $Me(CH_2)_5CO$ | O-Bn | m.p. 60 - 61°C |
| 148 | 4-F | H | H | $NHCH_2CH_2$(4-Ph-Ph) | m.p. 115-116°C |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 149 | 4-F | H | H | $NHCH_2CH_2$(4-PhO-Ph) | m.p. 48 - 49°C |
| 150 | 4-F | H | H | $OCH_2CH_2$(4-t-Bu-cyclohexyl) | m.p. 189-192°C (hydrochloride) |
| 151 | 2-F | H | H | O-cyclopentyl | m.p. 173-174°C (hydrochloride) |
| 152 | 2-F | H | H | O-cyclohexyl | m.p. 153-156°C (hydrochloride) |
| 153 | 2-F | H | H | $OCH_2CH=CHCH_2CH_2Me$ | m.p. 107-109°C (hydrochloride) |
| 154 | 2-F | H | H | $OCH_2C\equiv CCH_2CH_2Me$ | m.p. 123-125°C (hydrochloride) |
| 155 | 2-F | H | H | O-n-octyl | m.p. 103-105°C (hydrochloride) |
| 156 | 2-F | H | H | $OCH_2CH_2O(CH_2)_3Me$ | m.p. 102-105°C (hydrochloride) |
| 157 | 2-F | H | H | $OCH_2CH_2OCH_2CH_2OMe$ | m.p. 77 - 79°C (hydrochloride) |
| 158 | 2-F | H | H | O-cyclooctyl | m.p. 141-143°C (hydrochloride) |
| 159 | 2-F | H | H | $OCH(CH_3)$-n-pentyl | m.p. 89 - 91°C (hydrochloride) |
| 160 | 2-F | H | H | $OCH_2CH=CHCH=CHMe$ | m.p. 85 - 89°C (hydrochloride) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 161 | 2-F | H | H | $OCH_2CH_2Ph$ | m.p. 108-110°C (hydrochloride) |
| 162 | 2-F | H | H | $OCH_2COPh$ | m.p. 135-138°C (hydrochloride) |
| 163 | 2-F | H | H | O-cyclohexyl | m.p. 136-138°C (DSA salt) |
| 164 | 2-F | H | H | O-cyclohexyl | m.p. 161-162°C (TsOH salt) |
| 165 | 2-F | H | MeCO | O-cyclohexyl | m.p. 66 - 69°C |
| 166 | 2-F | H | $CH_3(CH_2)_5CO$ | O-cyclohexyl | $n_D$: 1.4928 (21°C) |
| 167 | 2-F | H | H | O-i-Pr | m.p. 156-158°C (hydrochloride) |
| 168 | 4-F | H | H | OH | m.p. 243-245°C(decomp.) (racemic modification) |
| 169 | 4-F | H | H | OH | m.p. 253-257°C (decomp.) (L-form) |
| 170 | 4-F | H | H | OH | m.p. 260-267°C (decomp.) (D-form) |
| 171 | 2-F | H | H | OH | m.p. 243-246°C (decomp.) |
| 172 | 3-F | H | H | OH | m.p. 240-250°C (decomp.) |

- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 173 | $2,4\text{-}F_2$ | H | H | OH | m.p. 256-259°C (decomp.) |
| 174 | $4\text{-}CF_3$ | H | H | OH | m.p. 205-208°C (decomp.) |
| 175 | $3,4\text{-}F_2$ | H | H | OH | m.p. 225-228°C (decomp.) |
| 176 | $4\text{-}CH_3O$ | H | H | OH | m.p. 215-218°C (decomp.) |
| 177 | $4\text{-}CH_3$ | H | H | OH | m.p. 238-240°C (decomp.) |
| 178 | 4-Cl | H | H | OH | m.p. 259-263°C (decomp.) |
| 179 | 4-OH | H | H | OH | m.p. 320-325°C (decomp.) |
| 180 | 4-F | H | H | O-Bn | m.p. 31-32°C |
| 181 | 4-F | H | H | O-Bn | m.p. 158-159°C (TsOH salt) |
| 182 | $2,4\text{-}F_2$ | H | H | O-Bn | m.p. 121-134°C (TsOH salt) |
| 183 | $2,4\text{-}F_2$ | H | H | O-Bn | paste |
| 184 | 2-F | H | H | O-Bn | paste |
| 185 | 3-F | H | H | O-Bn | paste |



- Cont'd -

Table 1 (Cont'd)

| No. | Xm | $R^1$ | $R^2$ | $R^3$ | Physical property |
|---|---|---|---|---|---|
| 186 | 4-$CF_3$ | H | H | O-Bn | m.p. 165-168°C (TsOH salt) |
| 187 | 4-$CF_3$ | H | H | O-Bn | paste |
| 188 | 3,4-$F_2$ | H | H | O-Bn | m.p. 153-154°C (TsOH salt) |
| 189 | 3,4-$F_2$ | H | H | O-Bn | paste |
| 190 | 4-$CH_3$ | H | H | O-Bn | m.p. 148-150°C (TsOH salt) |
| 191 | 4-$CH_3$ | H | H | O-Bn | paste |
| 192 | 2-F | H | H | O-Bn | m.p. 138-140°C (TsOH salt) |
| 193 | 4-F | H | H | OEt | m.p. 130-131°C (hydrochloride) |
| 194 | 4-F | H | H | OH | m.p. 220-225°C (decomp.) (hydrochloride) |
| 195 | 4-F | H | H | OK | m.p. 240-250°C (decomp.) |
| 196 | 2-F | H | H | OMe | m.p. 159-160°C (hydrochloride) |
| 197 | 2-F | H | H | OEt | m.p. 110-113°C (hydrochloride) |

Table 2 shows NMR data of the compounds having a physical property expressed by the word "paste" in Table 1.

Table 2

| No. | $CDCl_3$/TMS, δ value (ppm) |
|---|---|
| 8 | 2.72 (1H, m), 2.82 (1H, m), 2.94 (1H, m), 3.05 (2H, m), 3.12 (1H, m), 3.25 (1H, m), 3.53 (1H, m), 3.76 (2H, m), 3.95 (1H, m), 6.88 (3H, m), 7.00 (2H, m), 7.16 (2H, m), 7.27 (2H, m). |
| 11 | 2.87 (1H, dd), 3.01 (1H, dd), 3.72 (1H, dd), 5.09 (2H, m), 6.94 (2H, m), 7.07 (4H, m), 7.27 (2H, m). |
| 14 | 1.41 (9H, s), 2.83 (1H, dd), 2.99 (1H, dd), 3.57 (1H, dd), 6.98 (2H, m), 7.18 (2H, m). |
| 15 | 0.88 (6H, m), 1.15-1.75 (3H, m), 2.86 (1H, dd), 3.02 (1H, dd), 3.68 (1H, dd), 3.96 (1H, m), 4.12 (1H, m), 7.01 (2H, m), 7.16 (2H, m). |
| 16 | 2.88 (1H, dd), 3.08 (1H, dd), 3.81 (1H, dd), 4.56 (2H, m), 6.99 (2H, m), 7.16 (2H, m). |
| 17 | 2.87 (1H, dd), 3.00 (1H, dd), 3.72 (1H, dd), 5.02 (2H, m), 6.97 (2H, m), 7.13 (2H, m). |
| 27 | 1.31 (9H, s), 2.93 (2H, m), 3.55 (1H, t), 3.60 (1H, d), 3.76 (1H, d), 5.07 (2H, m), 6.90 (2H, m), 7.05 (2H, m), 7.14 (2H, d), 7.24 (2H, m), 7.30 (2H, d), 7.35 (3H, m). |
| 29 | 1.40 (9H, s), 3.03 (2H, m), 4.50 (1H, dd), 5.09 (2H, m), 5.24 (1H, d), 6.95 (2H, m), 7.10 (2H, m), 7.34 (5H, m). |

- Cont'd -

Table 2 (Cont'd)

| No. | $CDCl_3$/TMS, δ value (ppm) |
|---|---|
| 30 | 0.89 (6H, m), 1.12 (0.5H, m), 1.32 (0.5H, m), 1.48 (1H, m), 1.60 (1H, m), 3.09 (2H, m), 3.93 (1H, m), 4.11 (1H, m), 4.62 (1H, m), 5.09 (2H, m), 5.22 (1H, d), 6.95 (2H, m), 7.06 (2H, m), 7.35 (5H, m). |
| 32 | 1.42 (9H, s), 3.07 (2H, m), 4.59 (1H, m), 4.74 (2H, m), 4.98 (1H, m), 6.11 (1H, dt), 6.59 (1H, d), 6.93 (2H, m), 7.08 (4H, m), 7.35 (2H, m). |
| 33 | 1.42 (9H, s), 3.08 (2H, m), 4.36 (2H, t), 4.56 (1H, m), 4.74 (2H, m), 4.97 (1H, m), 6.08 (1H, m), 6.11 (1H, m), 6.58 (1H, d), 6.92 (4H, m), 7.09 (2H, m), 7.35 (2H, m). |
| 50 | 1.40 (9H, s), 1.59-1.90 (4H, m), 2.68-2.82 (1H, m), 2.89-2.92 (2H, dd), 2.98-3.08 (1H, m), 3.64 (1H, d), 4.30 (1H, d), 4.77 (1H, t), 5.09 (1H, d), 5.30-5.39 (1H, m), 6.88-6.97 (2H, m), 7.17-7.25 (2H, m), 7.28-7.37 (5H, m). |
| 51 | 1.60-1.88 (4H, m), 2.45-2.53 (1H, m), 2.70-2.82 (2H, m), 2.87-2.95 (1H, m), 3.63 (1H, d), 3.96 (1H, d), 4.35 (1H, t), 5.15 (2H, d), 6.95-7.02 (2H, m), 7.10-7.18 (2H, m), 7.27-7.36 (5H, m). |
| 54 | 2.68-2.74 (1H, m), 3.20-3.25 (1H, m), 3.62-3.66 (1H, m), 4.09 (2H, s), 5.18 (2H, s), 6.97-7.02 (2H, m), 7.15-7.19 (2H, m), 7.32-7.38 (5H, m), 7.78 (1H, s). |
| 67 | 0.93 (3H, t), 1.58-1.65 (6H, m), 2.85-2.90 (1H, m), 3.01-3.09 (1H, m), 3.69-3.72 (1H, m), 4.09-4.12 (2H, q), 6.96-7.03 (2H, m), 7.16-7.20 (2H, m). |
| 68 | 0.88 (3H, t), 1.28 (12H, m), 2.87 (1H, m), 3.05 (1H, m), 3.70 (1H, m), 4.10 (2H, t), 6.99 (2H, m), 7.15 (2H, m). |

- Cont'd -

Table 2

| No. | $CDCl_3$/TMS, δ value (ppm) |
|---|---|
| 69 | 1.58 (8H, m), 2.85 (1H, m), 3.00 (1H, m), 3.65 (1H, m), 5.18 (1H, m), 6.98 (2H, m), 7.17 (2H, m). |
| 70 | 2.82 (1H, m), 2.90 (2H, t), 2.98 (1H, m), 3.66 (1H, m), 4.29 (2H, t), 7.00 (8H, m). |
| 71 | 2.90 (1H, m), 3.05 (1H, m), 3.72 (1H, m), 4.60 (2H, d), 5.32 (2H, m), 5.90 (1H, m), 6.98 (2H, m), 7.17 (2H, m). |
| 72 | 2.49 (1H, s), 2.90 (1H, m), 3.10 (1H, m), 3.73 (1H, m), 4.71 (2H, s), 6.98 (2H, m), 7.17 (2H, m). |
| 73 | 0.92 (3H, t), 1.38 (2H, m), 1.56 (4H, m), 2.90 (1H, m), 3.04 (1H, m), 3.45 (2H, t), 3.60 (2H, t), 3.73 (1H, m), 4.26 (2H, t), 6.98 (2H, m), 7.18 (2H, m). |
| 74 | 1.33 (9H s), 2.71 (2H, t), 2.88 (1H, m), 3.02 (1H, m), 3.71 (1H, m), 4.21 (2H, t), 6.98 (2H, m), 7.20 (2H, m). |
| 75 | 2.85 (1H, m), 2.98 (1H, m), 3.11 (2H, t), 3.65 (1H, m), 4.26 (2H, m), 6.97 (2H, m), 7.14 (2H, m), 7.30 (5H, m). |
| 97 | 1.30 (3H, t), 1.50 (2H, br), 2.89 (1H, q), 3.14 (1H, q), 3.80 (1H, q), 4.24 (2H, q), 4.65 (2H, dd), 7.01 (2H, q), 7.24 (2H, q). |
| 98 | 1.51 (2H, br), 2.67 (2H, t), 2.88 (1H, q), 3.09 (1H, q), 3.78 (1H, q), 4.30 (2H, q), 7.02 (2H, q), 7.19 (2H, q). |
| 107 | 0.88 (3H, t), 1.15-1.50 (10H, m), 3.30 (1H, q), 3.45 (1H, q), 4.03 (2H, q), 4.35 (1H, br), 6.97 (2H, q), 7.26 (2H, q), 8.80 (3H, br). |

- Cont'd -

Table 2

| No. | $CDCl_3$/TMS, δ value (ppm) |
|---|---|
| 112 | 0.86 (3H, t) 1.10-1.50 (8H, m), 3.07 (1H, m), 3.25 (1H, m), 4.02 (2H, t), 4.23 (1H, br), 7.15 (2H, m), 7.31 (2H, m), 8.70 (3H, br). (DMSO-$d_6$) |
| 113 | 0.86 (3H, t), 1.11-1.50 (10H, m), 3.08 (1H, m), 3.22 (1H, m), 4.02 (2H, m), 4.25 (1H, br), 7.15 (2H, m), 7.28 (2H, m), 8.60 (3H, br). (DMSO-$d_6$) |
| 129 | 2.75 (6H, s), 3.20 (1H, t), 4.35 (2H, m), 4.52 (1H, m), 7.15 (2H, m), 7.34 (2H, m), 8.70 (3H, br). (DMSO-$d_6$) |
| 183 | 2.89-2.94 (1H, m), 3.03-3.06 (1H, m), 3.74-3.78 (1H, m), 5.12 (2H, s), 6.73-6.78 (2H, m), 7.29-7.36 (6H, m). |
| 184 | 2.94 (1H, dd), 3.11 (1H, dd), 3.81 (1H, dd), 5.13 (2H, m), 6.95-7.32 (9H, m). |
| 185 | 2.89 (1H, dd), 3.07 (1H, dd), 3.76 (1H, dd), 5.14 (2H, m), 6.80-6.92 (3H, m), 7.16-7.40 (6H, m). |
| 187 | 2.93-2.98 (1H, m), 3.09-3.12 (1H, m), 3.76-3.79 (1H, m), 5.08-5.18 (2H, m), 7.23-7.28 (6H, m), 7.34-7.48 (3H, m). |
| 189 | 2.83-2.88 (1H, m), 2.97-3.02 (1H, m), 3.71-3.74 (1H, m), 5.07-5.18 (2H, dd), 6.83-6.87 (1H, m), 6.99-7.26 (3H, m), 7.31-7.51 (4H, m). |
| 191 | 2.31 (3H, s), 2.83-2.88 (1H, m), 3.02-3.06 (1H, m), 3.73-3.76 (1H, m), 5.10-5.17 (2H, m), 7.01-7.08 (4H, m), 7.29-7.39 (5H, m). |

EXAMPLES OF THE INVENTION

The present invention is concretely illustrated with the following examples, formulation examples and test examples, which should not be construed as limiting the scope of the invention.

Example 1

Production of N-(p-toluenesulfonyl)-4-fluorophenylalanine (compound 1)

In 10 ml of ethanol was dissolved 0.35 g of N-(p-toluenesulfonyl)-4-fluorophenylalanine benzyl ester, followed by adding thereto 0.08 g of 10% Pd-C, and the resulting mixture was subjected to hydrogenation at ordinary temperature and atmospheric pressure. After completion of the reaction, the catalyst was filtered off and the filtrate was concentrated under reduced pressure. Ether was added to the concentrate to effect crystallization and the crystals were filtered and then washed with ether to obtain 0.24 g of crystals of the desired compound.

Physical property: m.p. 142 - 143°C.

Yield: 87%.

Example 2

Production of 4-fluorophenylalanine cyclohexylamide acetate (compound 6)

In a mixed solvent of ethanol, acetic acid and water in volumes of 10 ml, 1 ml and 1 ml, respectively,

was dissolved 0.45 g of N-(benzyloxycarbonyl)-4-fluorophenylalanine cyclohexylamide, followed by adding thereto 0.18 g of 10% Pd-C, and the resulting mixture was subjected to hydrogenation at ordinary temperature and atmospheric pressure. After completion of the reaction, the catalyst was filtered off and the filtrate was concentrated under reduced pressure. Hexane was added to the concentrate to effect crystallization and the crystals were filtered and then washed with hexane to obtain 0.26 g of crystals of the desired compound.

Physical property: m.p. 115 - 116°C.

Yield: 72%.

Example 3

Production of N-(tert-butoxycarbonyl)-4-fluorophenylalanine benzylamide (compound 9)

In 15 ml of dried tetrahydrofuran were dissolved 0.52 g of N-(tert-butoxycarbonyl)-4-fluorophenylalanine and 0.26 ml of triethylamine, followed by adding thereto 0.25 ml of isobutyl chloroformate under ice-cooling. After stirring for 30 minutes, 0.21 ml of benzylamine was added and the resulting mixture was stirred at room temperature for another 3 hours. After completion of the reaction, the reaction mixture was poured into ice water and the desired compound was extracted with ethyl acetate. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were

washed with hexane to obtain 0.49 g of crystals of the desired compound.

Physical property: m.p. 169 - 170°C.

Yield: 72%.

Example 4

Production of 4-fluorophenylalanine benzylamide (compound 10)

To 0.40 g of N-(tert-butoxycarbonyl)-4-fluorophenylalanine benzylamide was added 5 ml of trifluoroacetic acid, and the resulting mixture was stirred at room temperature for 1 hour. After completion of the reaction, the reaction mixture was poured into ice water and a saturated aqueous sodium hydrogencarbonate solution was added, and the desired compound was extracted with ethyl acetate. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with hexane to obtain 0.26 g of crystals of the desired compound.

Physical property: m.p. 67 - 68°C.

Yield: 91%.

Example 5

Production of N-(benzyloxycarbonyl)-4-fluorophenylalanine cyclohexylamide (compound 19)

In 15 ml of dried tetrahydrofuran were dissolved 1.0 g of N-(benzyloxycarbonyl)-4-fluorophenyl-

alanine and 0.44 ml of triethylamine, followed by adding thereto 0.42 ml of isobutyl chloroformate under ice-cooling. After stirring for 30 minutes, 0.4 ml of cyclohexylamine was added and the resulting mixture was stirred at room temperature for another 3 hours. After completion of the reaction, the reaction mixture was poured into ice water and the desired compound was extracted with ethyl acetate. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with hexane to obtain 0.78 g of crystals of the desired compound.

Physical property: m.p. 183 - 184°C.

Yield: 62%.

Example 6

Production of N-(p-toluenesulfonyl)-4-fluorophenylalanine benzyl ester (compound 23)

In 30 ml of dried dichloromethane were dissolved 1.5 g of 4-fluorophenylalanine benzyl ester p-toluenesulfonate and 1.00 ml of triethylamine, followed by adding thereto 0.71 g of p-toluenesulfonyl chloride under ice-cooling. After stirring at room temperature for 24 hours, the reaction mixture was poured into ice water and the desired compound was extracted with dichloromethane. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with ether to obtain 0.65 g of crystals of the desired compound.

Physical property: m.p. 130 - 131°C.

Yield: 45%.

Example 7

Production of N-(4-tert-butylbenzyl)-4-fluorophenylalanine benzyl ester (compound 27)

In 15 ml of tetrahydrofuran were dissolved 1.0 g of 4-fluorophenylalanine benzyl ester p-toluenesulfonate and 0.65 ml of triethylamine, followed by adding thereto 0.53 g of 4-tert-butylbenzyl bromide, and the resulting mixture was stirred at room temperature for 24 hours. After completion of the reaction, the desired compound was extracted with ethyl acetate, and the organic layer was washed with a saturated aqueous sodium hydrogencarbonate solution, dried, and then concentrated under reduced pressure. The oil thus obtained was purified by a silica gel column chromatography to obtain 0.18 g of the desired compound.

Physical property: paste. Yield: 19%.

NMR[$CDCl_3$/TMS, δ values (ppm)]

1.31(9H, s), 2.93(2H, m), 3.55(1H, t), 3.60(1H, d), 3.76(1H, d), 5.07(2H, m), 6.90(2H, m), 7.05(2H, m), 7.14(2H, d), 7.24(2H, m), 7.30(2H, d), 7.35(3H, m).

Example 8

Production of N-(benzyloxycarbonyl)-4-fluorophenylalanine isoamyl ester (compound 30)

In 15 ml of dried dichloromethane were dissolved 1.00 g of N-(benzyloxycarbonyl)-4-fluorophenylalanine, 0.07 g of dimethylaminopyridine and 0.69 ml of isoamyl alcohol, followed by adding thereto 0.66 g of 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride under ice-cooling. After stirring at room temperature for 24 hours, the reaction mixture was poured into ice water, and the desired compound was extracted with ethyl acetate. The organic layer was washed with 1N HCl, dried, and then concentrated under reduced pressure, and the oil thus obtained was purified by a silica gel column chromatography to obtain 1.16 g of the desired compound.

Physical property: paste. Yield: 95%.

NMR[$CDCl_3$/TMS, δ values (ppm)]

0.89(6H, m), 1.12(0.5H, m), 1.32(0.5H, m), 1.48(1H, m), 1.60(1H, m), 3.09(2H, m), 3.93(1H, m), 4.11(1H, m), 4.62(1H, m), 5.09(2H, m), 5.22(1H, d), 6.95(2H, m), 7.06(2H, m), 7.35(5H, m).

Example 9

Production of N-(benzyloxycarbonyl)-4-fluorophenylalanyl-piperidine-4-carboxylic acid (compound 40)

In 6 ml of aqueous ethanol was dissolved 0.5 g of ethyl N-(benzyloxycarbonyl)-4-fluorophenylalanyl-piperidine-4-carboxylate, followed by adding thereto

0.05 g of lithium hydroxide, and the resulting mixture was stirred at room temperature for 24 hours. After completion of the reaction, the reaction mixture was poured into ice water and acidified with 1N HCl, and the desired compound was extracted with ethyl acetate. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with ether to obtain 0.44 g of the desired compound.

Physical property: m.p. 180 - 181°C.

Yield: 94%.

Example 10

Production of N-(benzyloxycarbonyl)-4-fluorophenylalanyl-valine benzyl ester (compound 44)

In 40 ml of dried tetrahydrofuran were dissolved 2.0 g of N-(benzyloxycarbonyl)-4-fluorophenylalanine and 2.62 ml of triethylamine, and 0.83 ml of isobutyl chloroformate was added and then stirred for 30 minutes. Then, 2.39 g of valine benzyl ester p-toluenesulfonate was added, and the resulting mixture was stirred at room temperature for another 24 hours. After completion of the reaction, the reaction mixture was poured into ice water and the desired compound was extracted with ethyl acetate. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with hexane to obtain 0.63 g of crystals of the desired compound.

Physical property: m.p. 120 - 122°C.

Yield: 20%.

Example 11

Production of 4-fluorophenylalanyl-valine (compound 45)

In a mixed solvent of ethanol, acetic acid and water in volumes of 20 ml, 1 ml and 1 ml, respectively, was dissolved 1.00 g of N-(benzyloxycarbonyl)-4-fluorophenylalanyl-valine benzyl ester, followed by adding thereto 0.20 g of 10% Pd-C, and the resulting mixture was subjected to hydrogenation at ordinary temperature and atmospheric pressure. After completion of the reaction, the catalyst was filtered off and the filtrate was concentrated under reduced pressure. Ether was added to the concentrate to effect crystallization and the crystals were filtered and then washed with hexane to obtain 0.30 g of the desired compound.

Physical property: m.p. 142 - 145°C.

Yield: 54%.

Example 12

Production of 4-fluorophenylalanine (D,L-amino acid) (compound 168)

In 100 ml of ethanol was dissolved 1.44 g of metallic sodium, followed by adding thereto 12.38 g of diethyl acetamidomalonate and 8.24 g of 4-fluorobenzyl chloride, and the resulting mixture was stirred with

heating for 7 hours. After completion of the reaction, ice water was added to the reaction mixture and the crystals precipitated were filtered and washed with water to obtain 14.0 g of crystals. The crystals obtained were dissolved in 50 ml of a 47% aqueous hydrobromic acid solution and the resulting solution was stirred with heating for 8 hours. The reaction solution was neutralized with concentrated aqueous ammonia under ice-cooling, and the crystals thus precipitated were filtered and then washed with water to obtain 4.9 g of crystals of the desired compound.

Physical property: m.p. 253 - 257°C (decomp.).

Yield: 47%.

Example 13

Production of 4-fluorophenylalanine benzyl ester p-toluenesulfonate (TsOH salt, compound 181)

In 60 ml of toluene, 11.0 g of 4-fluorophenylalanine, 80 ml of benzyl alcohol and 12.6 g of p-toluenesulfonic acid monohydrate were stirred with heating for 6 hours by using a Dean-Stark trap. After completion of the reaction, 100 ml of ether was added to the reaction mixture and the crystals precipitated were filtered and then washed with hexane to obtain 23.2 g of crystals of the desired compound.

Physical property: m.p. 158 - 159°C.

Yield: 87%.

Reference Example 1

Production of N-(benzyloxycarbonyl)-4-fluorophenylalanine

In 30 ml of a 2M aqueous sodium hydroxide solution was dissolved 4.9 g of 4-fluorophenylalanine, followed by adding dropwise thereto 5.0 g of benzyloxycarbonyl chloride under ice-cooling, and the resulting solution was stirred at 10°C for 3 hours. The reaction solution was washed with ether, after which the aqueous layer was acidified with 1N HCl and the desired compound was extracted with ethyl acetate. The organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with ether to obtain 7.13 g of crystals of the desired compound.

Physical property: m.p. 120 - 122°C.

Yield: 84%.

Reference Example 2

Production of N-(tert-butoxycarbonyl)-4-fluorophenylalanine

In 80 ml of a 1M aqueous sodium hydroxide solution was dissolved 10.1 g of 4-fluorophenylalanine, followed by adding dropwise thereto 13.2 g of di-tert-butyl dicarbonate under ice-cooling, and the resulting solution was stirred overnight at room temperature. The reaction solution was washed with ether, after which the aqueous layer was acidified with citric acid and the desired compound was extracted with ethyl acetate. The

organic layer was dried and then concentrated under reduced pressure, and the crystals thus obtained were washed with hexane to obtain 4.9 g of the desired compound.

Physical property: m.p. 253 - 257°C (decomp.).

Yield: 47%.

Formulation examples are described below. In the formulation examples, parts are all by weight.

Formulation Example 1

| | |
|---|---|
| Each compound of the invention | 50 parts |
| Xylene | 40 parts |
| Mixture of polyoxyethylene nonylphenyl ether and alkylbenzenesulfonate | 10 parts |

An emulsifiable concentrate was prepared by mixing uniformly the above ingredients to effect dissolution.

Formulation Example 2

| | |
|---|---|
| Each compound of the invention | 0.5 part |
| Xylene | 0.8 part |
| Illuminating kerosine | 98.7 parts |

An oil formulation was prepared by mixing uniformly the above ingredients to effect dissolution.

Formulation Example 3

| | |
|---|---|
| Each compound of the invention | 3 parts |
| Clay powder | 82 parts |
| Diatomaceous earth powder | 15 parts |

A dust was prepared by mixing uniformly and grinding the above ingredients.

Formulation Example 4

| | |
|---|---|
| Each compound of the invention | 5 parts |
| Mixed powder of bentonite and clay | 90 parts |
| Calcium stearate | 1 part |

Granules were prepared by mixing the above ingredients uniformly, and kneading the resulting mixture together with a suitable amount of water, followed by granulation and drying.

Formulation Example 5

| | |
|---|---|
| Each compound of the invention | 20 parts |
| Mixture of kaolin and synthetic, high-dispersion silicic acid | 75 parts |
| Mixture of polyoxyethylene nonylphenyl ether and calcium alkylbenzenesulfonate | 5 parts |

A wettable powder was prepared by mixing uniformly and grinding the above ingredients.

Test Example 1

Controlling effect on apple Alternaria leaf spot

The leaves of apple plants were sufficiently sprayed with a 200 ppm liquid chemical containing each compound of the present invention as active ingredient, and then inoculated with a suspension of spores of Alternaria leaf spot fungus (Alternaria mali) by spaying. The plants were placed in a moist chamber at 15°C for 1 day and then in a room thermostated at 15°C for 3 days, to cause the disease sufficiently. Thereafter, the lesion area of each leaf was measured and then compared with that on the untreated plot, whereby the effect was judged according to the following criterion.

| Effect | Controlling degree (%) |
|---|---|
| A | 100 - 95 |
| B | 94 - 80 |
| C | 79 - 60 |
| D | 59 - 0 |
| - | no phytotoxicity |

The results obtained are shown in Table 3.

Test Example 2

Controlling effect on apple scab

Potted apple plants were sufficiently sprayed with a 200 ppm liquid chemical containing each compound of the present invention as active ingredient. Twenty-four hours after the spraying, the plants were inoculated with a suspension of spores of scab fungus

(Venturia inaequalis) by spraying. The plants were placed in a moist chamber at 17°C for 1 day and then in a room thermostated at 17°C for 10 days, to cause the disease sufficiently. Thereafter, the lesion area of each leaf was measured and then compared with that on the untreated plot, whereby the effect was judged according to the same criterion as described in Test Example 1. The results obtained are shown in Table 3.

Table 3

| No. | Concen-tration (ppm) | Test Example 1 | Test Example 2 | Phyto-toxicity |
|---|---|---|---|---|
| 1 | 200 | D | B | - |
| 2 | 200 | D | D | - |
| 3 | 200 | D | D | - |
| 4 | 200 | D | B | - |
| 5 | 200 | D | D | - |
| 6 | 200 | D | D | - |
| 7 | 200 | B | D | - |
| 8 | 200 | A | D | - |
| 9 | 200 | C | C | - |
| 10 | 200 | B | B | - |
| 11 | 200 | A | D | - |
| 12 | 200 | A | D | - |
| 13 | 200 | A | D | - |
| 14 | 200 | A | D | - |
| 15 | 200 | A | A | - |
| 16 | 200 | B | D | - |
| 17 | 200 | A | D | - |
| 18 | 200 | D | D | - |
| 19 | 200 | D | D | - |
| 20 | 200 | D | D | - |
| 21 | 200 | D | D | - |
| 22 | 200 | D | D | - |
| 23 | 200 | D | B | - |
| 24 | 200 | D | C | - |
| 25 | 200 | D | D | - |
| 26 | 200 | D | B | - |
| 27 | 200 | D | D | - |
| 28 | 200 | D | D | - |
| 29 | 200 | B | D | - |

- Cont'd -

Table 3 (Cont'd)

| No. | Concentration (ppm) | Test Example 1 | Test Example 2 | Phytotoxicity |
|---|---|---|---|---|
| 30 | 200 | C | D | - |
| 31 | 200 | B | D | - |
| 32 | 200 | A | D | - |
| 33 | 200 | B | D | - |
| 34 | 200 | D | D | - |
| 35 | 200 | D | D | - |
| 36 | 200 | D | D | - |
| 37 | 200 | D | D | - |
| 38 | 200 | D | D | - |
| 39 | 200 | D | D | - |
| 40 | 200 | D | D | - |
| 41 | 200 | D | D | - |
| 42 | 200 | D | C | - |
| 43 | 200 | D | D | - |
| 44 | 200 | D | D | - |
| 45 | 200 | A | D | - |
| 46 | 200 | D | D | - |
| 47 | 200 | A | D | - |
| 48 | 200 | C | D | - |
| 49 | 200 | A | D | - |
| 50 | 200 | C | D | - |
| 51 | 200 | A | D | - |
| 52 | 200 | A | D | - |
| 53 | 200 | D | D | - |
| 54 | 200 | C | D | - |
| 55 | 200 | A | A | - |
| 56 | 200 | A | A | - |
| 57 | 200 | C | C | - |
| 96 | 200 | A | C | - |

- Cont'd -

Table 3 (Cont'd)

| No. | Concen-tration (ppm) | Test Example 1 | Test Example 2 | Phyto-toxicity |
|---|---|---|---|---|
| 97 | 200 | A | D | - |
| 98 | 200 | A | D | - |
| 99 | 200 | A | D | - |
| 100 | 200 | C | D | - |
| 101 | 200 | D | C | - |
| 102 | 200 | A | D | - |
| 103 | 200 | A | D | - |
| 104 | 200 | D | D | - |
| 105 | 200 | A | D | - |
| 106 | 200 | B | A | - |
| 107 | 200 | C | A | - |
| 108 | 200 | A | D | - |
| 109 | 200 | C | C | - |
| 110 | 200 | B | C | - |
| 111 | 200 | A | D | - |
| 112 | 200 | D | C | - |
| 113 | 200 | D | D | - |
| 114 | 200 | A | D | - |
| 115 | 200 | D | D | - |
| 116 | 200 | B | D | - |
| 117 | 200 | C | D | - |
| 118 | 200 | A | D | - |
| 119 | 200 | A | D | - |
| 120 | 200 | A | D | - |
| 121 | 200 | A | A | - |
| 122 | 200 | A | D | - |
| 123 | 200 | A | D | - |
| 124 | 200 | A | A | - |
| 125 | 200 | A | A | - |

- Cont'd -

Table 3 (Cont'd)

| No. | Concentration (ppm) | Test Example 1 | Test Example 2 | Phytotoxicity |
|---|---|---|---|---|
| 126 | 200 | A | A | - |
| 127 | 200 | A | A | - |
| 128 | 200 | A | D | - |
| 129 | 200 | A | D | - |
| 130 | 200 | A | C | - |
| 131 | 200 | A | D | - |
| 132 | 200 | C | D | - |
| 133 | 200 | A | D | - |
| 134 | 200 | B | D | - |
| 135 | 200 | A | D | - |
| 136 | 200 | A | D | - |
| 137 | 200 | C | B | - |
| 138 | 200 | A | A | - |
| 139 | 200 | A | D | - |
| 140 | 200 | A | A | - |
| 141 | 200 | D | D | - |
| 142 | 200 | B | D | - |
| 143 | 200 | A | A | - |
| 144 | 200 | D | D | - |
| 145 | 200 | A | D | - |
| 146 | 200 | D | D | - |
| 147 | 200 | A | D | - |
| 148 | 200 | A | D | - |
| 149 | 200 | A | A | - |
| 150 | 200 | A | A | - |
| 151 | 200 | A | D | - |
| 152 | 200 | A | B | - |
| 153 | 200 | A | D | - |
| 154 | 200 | C | D | - |

- Cont'd -

Table 3 (Cont'd)

| No. | Concentration (ppm) | Test Example 1 | Test Example 2 | Phytotoxicity |
|---|---|---|---|---|
| 155 | 200 | A | D | - |
| 156 | 200 | A | A | - |
| 157 | 200 | A | D | - |
| 158 | 200 | A | B | - |
| 159 | 200 | A | D | - |
| 160 | 200 | A | D | - |
| 161 | 200 | B | C | - |
| 162 | 200 | A | D | - |
| 163 | 200 | A | D | - |
| 164 | 200 | A | A | - |
| 165 | 200 | A | D | - |
| 166 | 200 | B | D | - |
| 167 | 200 | A | C | - |
| 168 | 200 | B | B | - |
| 169 | 200 | C | C | - |
| 170 | 200 | A | B | - |
| 171 | 200 | A | D | - |
| 172 | 200 | A | C | - |
| 173 | 200 | A | D | - |
| 174 | 200 | C | D | - |
| 175 | 200 | C | D | - |
| 176 | 200 | B | D | - |
| 177 | 200 | D | D | - |
| 180 | 200 | A | B | - |
| 181 | 200 | C | A | - |
| 182 | 200 | C | D | - |
| 183 | 200 | A | A | - |
| 184 | 200 | A | C | - |
| 185 | 200 | A | D | - |

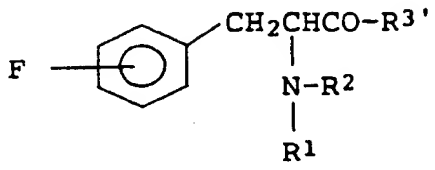
- Cont'd -

Table 3 (Cont'd)

| No. | Concen-tration (ppm) | Test Example 1 | Test Example 2 | Phyto-toxicity |
|---|---|---|---|---|
| 186 | 200 | D | D | - |
| 187 | 200 | D | D | - |
| 188 | 200 | C | A | - |
| 189 | 200 | D | D | - |
| 190 | 200 | D | D | - |
| 191 | 200 | D | D | - |
| 192 | 200 | A | D | - |
| 193 | 200 | A | D | - |
| 194 | 200 | A | D | - |
| 195 | 200 | B | D | - |
| 196 | 200 | A | D | - |
| 197 | 200 | A | D | - |

CLAIMS

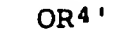
1. A phenylalanine derivative represented by the general formula (Ia):



(Ia)

wherein $R^1$ is a hydrogen atom or a $(C_1-C_8)$alkyl group, $R^2$ is a hydrogen atom; a $(C_1-C_8)$alkyl group; a $(C_1-C_6)$-alkoxycarbonyl group; an unsubstituted $(C_1-C_6)$alkyl-carbonyl group; a substituted $(C_1-C_6)$alkylcarbonyl group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl$(C_1-C_6)$alkyl group; a substituted phenyl$(C_1-C_6)$-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, $(C_1-C_6)$alkyl groups, halo$(C_1-C_6)$alkyl groups, $(C_1-C_6)$alkoxy groups, halo$(C_1-C_6)$alkoxy groups, carboxyl group, $(C_1-C_6)$alkoxycarbonyl groups, $(C_1-C_6)$alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl group; a substituted phenylcarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, $(C_1-C_6)$alkyl groups, halo$(C_1-C_6)$alkyl groups, $(C_1-C_6)$alkoxy groups, halo$(C_1-C_6)$alkoxy groups, carboxyl group, $(C_1-C_6)$alkoxy-

carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylsulfonyl group; a substituted phenylsulfonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group; or a substituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^1$ and $R^2$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, or a phthaloyl group, and $R^{3'}$ is a group represented by the formula:



(wherein $R^{4'}$ is a hydrogen atom; a ($C_3$-$C_{18}$)alkyl group; a halo($C_1$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; a cyclo($C_3$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group; a hydroxy($C_1$-$C_6$)-alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)-alkylthio($C_1$-$C_6$)alkyl group; a carboxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; a cyano($C_1$-$C_6$)alkyl group; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsub-

stituted phenyl($C_2$-$C_6$)alkenyl group; a substituted phenyl($C_2$-$C_6$)alkenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylthio-($C_1$-$C_6$)alkyl group; a substituted phenylthio($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl($C_1$-$C_6$)alkyl group; a substituted phenyl-carbonyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are

selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom, provided that when each of $R^1$ and $R^2$ is a hydrogen atom, $R^{4'}$ is other than hydrogen atom, tert-butyl group and benzyl group), a group represented by the formula:

$$N(R^5)-R^6$$

(wherein $R^5$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; an unsubstituted cyano($C_1$-$C_6$)alkyl group; a substituted cyano($C_1$-$C_6$)alkyl group having one or more substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups and phenyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)-alkoxy($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)-alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or

different and are selected from ($C_1$-$C_6$)alkyl groups; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxy group; a substituted phenyl($C_1$-$C_6$)alkyloxy group having on the ring 1 to 5 substituents which may

be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; or a guanidyl-($C_1$-$C_6$)alkyl group, and $R^6$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group or a ($C_2$-$C_6$)alkenyl group, $R^5$ and $R^6$ being able to be taken together to represent a ($C_1$-$C_6$)-alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, and said ($C_1$-$C_6$)alkylene group being able to form a ring and have on the ring one or more substituents which may be the same or different and are selected from the group consisting of ($C_1$-$C_6$)alkyl groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, phenyl group, phenyl($C_1$-$C_6$)alkyloxycarbonyl groups and phenyl($C_1$-$C_6$)alkyloxy groups, provided that $R^1$, $R^2$, $R^5$ and $R^6$ are not hydrogen atoms at the same time, and that when $R^1$ is a tert-butoxycarbonyl group and $R^5$ is a benzyl group, $R^6$ is other than methyl group) or a group represented by the formula:

$$NHCH(R^7)(CH_2)_nCOOR^8$$

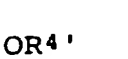
(wherein $R^7$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, a cyclo($C_3$-$C_8$)alkyl group, a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group, a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group, a hydroxy-

($C_1$-$C_6$)alkyl group, an amino($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^8$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, and n is 0 or 1, provided that when each of $R^1$ and $R^2$ is a hydrogen atom, $R^7$ is other than methyl group and isobutyl group, and that when $R^1$ is a benzyloxycarbonyl group, $R^7$ is a hydrogen atom and n is 0, $R^8$ is other than ethyl group).

2. A phenylalanine derivative according to claim 1, wherein $R^1$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^2$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl group; an unsubstituted ($C_1$-$C_6$)-alkylcarbonyl group; a substituted ($C_1$-$C_6$)alkylcarbonyl

group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl-($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl group; a substituted phenylcarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylsulfonyl group; a substituted phenylsulfonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group; or a substituted phenyl($C_1$-$C_6$)-

alkyloxycarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^1$ and $R^2$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, or a phthaloyl group, and $R^{3'}$ is a group represented by the formula:



(wherein $R^{4'}$ is a hydrogen atom; a ($C_3$-$C_{18}$)alkyl group; a halo($C_1$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; a cyclo($C_3$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group; a hydroxy($C_1$-$C_6$)-alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkylthio($C_1$-$C_6$)alkyl group; a carboxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; a cyano($C_1$-$C_6$)alkyl group; an

unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_2$-$C_6$)alkenyl group; a substituted phenyl($C_2$-$C_6$)alkenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of

halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylthio-($C_1$-$C_6$)alkyl group; a substituted phenylthio($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl($C_1$-$C_6$)alkyl group; a substituted phenyl-carbonyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl ($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom, provided that when each of $R^1$ and $R^2$ is a hydrogen atom, $R^{4'}$ is

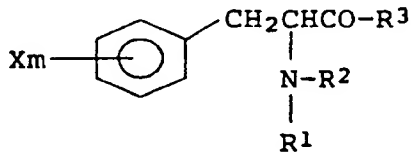
other than hydrogen atom, tert-butyl group and benzyl group).

3. A phenylalanine derivative according to claim 1 or 2, which is an optically active substance.

4. A phenylalanine derivative according to claim 1, 2 or 3, which is a chemically acceptable salt.

5. A phenylalanine derivative according to claim 1 or 2, which is a coordination compound.

6. A fungicide for fruit gardening comprising as an active ingredient a phenylalanine derivative represented by the general formula (I):



(I)

wherein $R^1$ is a hydrogen atom or a $(C_1-C_8)$alkyl group, $R^2$ is a hydrogen atom; a $(C_1-C_8)$alkyl group; a $(C_1-C_6)$-alkoxycarbonyl group; an unsubstituted $(C_1-C_6)$alkyl-carbonyl group; a substituted $(C_1-C_6)$alkylcarbonyl group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl$(C_1-C_6)$alkyl group; a substituted phenyl$(C_1-C_6)$-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, $(C_1-C_6)$alkyl groups, halo$(C_1-C_6)$alkyl groups, $(C_1-C_6)$alkoxy groups, halo$(C_1-C_6)$alkoxy groups, carboxyl group, $(C_1-C_6)$alkoxycarbonyl groups, $(C_1-C_6)$alkylene-

dioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl group; a substituted phenylcarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylsulfonyl group; a substituted phenylsulfonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group; or a substituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^1$ and $R^2$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group

which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, or a phthaloyl group, $R^3$ is a group represented by the formula:



(wherein $R^4$ is a hydrogen atom; a ($C_1$-$C_{18}$)alkyl group; a halo($C_1$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; a cyclo($C_3$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group; a hydroxy($C_1$-$C_6$)-alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)-alkylthio($C_1$-$C_6$)alkyl group; a carboxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; a cyano($C_1$-$C_6$)alkyl group; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-

alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_2$-$C_6$)alkenyl group; a substituted phenyl($C_2$-$C_6$)alkenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylthio-($C_1$-$C_6$)alkyl group; a substituted phenylthio($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group,

($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl($C_1$-$C_6$)alkyl group; a substituted phenylcarbonyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy group, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom), a group represented by the formula:

$$N(R^5)-R^6$$

(wherein $R^5$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; an unsubstituted cyano($C_1$-$C_6$)alkyl group; a substituted cyano($C_1$-$C_6$)alkyl group having one or more substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-

alkoxy groups and phenyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)-alkoxy($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)-alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; an unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyl group; a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-

dioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyloxy group; a substituted phenyl($C_1$-$C_6$)alkyloxy group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; or a guanidyl($C_1$-$C_6$)alkyl group, and $R^6$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group or a ($C_2$-$C_6$)alkenyl group, $R^5$ and $R^6$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, and said ($C_1$-$C_6$)alkylene group being able to form a ring and have on the ring one or more substituents which may be the same or different and are selected from the group consisting of ($C_1$-$C_6$)alkyl groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, phenyl group, phenyl-($C_1$-$C_6$)alkyloxycarbonyl groups and phenyl($C_1$-$C_6$)alkyloxy groups) or a group represented by the formula:

$$NHCH(R^7)(CH_2)_nCOOR^8$$

(wherein $R^7$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, a cyclo($C_3$-$C_8$)alkyl group, a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group, a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group, a hydroxy-

($C_1$-$C_6$)alkyl group, an amino($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^8$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, and n is 0 or 1), X is a halogen atom, a nitro group, a cyano group, a hydroxyl group, an amino group, a ($C_1$-$C_6$)alkyl group, a halo($C_1$-$C_6$)alkyl group or a ($C_1$-$C_6$)alkoxy group, and m is an integer of 1 or 2.

7. A fungicide for fruit gardening according to claim 6, wherein $R^1$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^2$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl group; an unsubstituted ($C_1$-$C_6$)-alkylcarbonyl group; a substituted ($C_1$-$C_6$)alkylcarbonyl

group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl-($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl group; a substituted phenylcarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylsulfonyl group; a substituted phenylsulfonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)-alkyloxycarbonyl group; or a substituted phenyl($C_1$-$C_6$)-

alkyloxycarbonyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group, $R^1$ and $R^2$ being able to be taken together to represent a ($C_1$-$C_6$)alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, or a phthaloyl group, $R^3$ is a group represented by the formula:

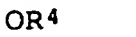
(wherein $R^4$ is a hydrogen atom; a ($C_1$-$C_{18}$)alkyl group; a halo($C_1$-$C_8$)alkyl group; a ($C_2$-$C_6$)alkenyl group; a ($C_2$-$C_6$)alkynyl group; a cyclo($C_3$-$C_8$)alkyl group; a cyclo($C_3$-$C_8$)alkyl($C_1$-$C_6$)alkyl group; a hydroxy($C_1$-$C_6$)-alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)-alkylthio($C_1$-$C_6$)alkyl group; a carboxy($C_1$-$C_6$)alkyl group; a ($C_1$-$C_6$)alkoxycarbonyl($C_1$-$C_6$)alkyl group; an unsubstituted amino($C_1$-$C_6$)alkyl group; a substituted amino($C_1$-$C_6$)alkyl group having 1 or 2 substituents which may be the same or different and are selected from ($C_1$-$C_6$)alkyl groups; a cyano($C_1$-$C_6$)alkyl group; an

unsubstituted phenyl group; a substituted phenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-dioxy groups, phenyl group and phenoxy group; an unsubstituted phenyl($C_2$-$C_6$)alkenyl group; a substituted phenyl($C_2$-$C_6$)alkenyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxy-carbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenoxy-($C_1$-$C_6$)alkyl group; a substituted phenoxy($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group

consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylthio($C_1$-$C_6$)alkyl group; a substituted phenylthio-($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo-($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)-alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; an unsubstituted phenylcarbonyl($C_1$-$C_6$)-alkyl group; a substituted phenylcarbonyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl-($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)-alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom), X is a halogen atom, a nitro group, a cyano group, a hydroxyl group, an amino group, a

($C_1$-$C_6$)alkyl group, a halo($C_1$-$C_6$)alkyl group or a ($C_1$-$C_6$)alkoxy group, and m is an integer of 1 or 2.

8. A fungicide for fruit gardening according to claim 7, wherein $R^1$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^2$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^3$ is a group represented by the formula:



(wherein $R^4$ is a hydrogen atom, a ($C_1$-$C_8$)alkyl group, a cyclo($C_3$-$C_8$)alkyl group, a ($C_2$-$C_6$)alkenyl group, a ($C_2$-$C_6$)alkynyl group, a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group, a ($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkoxy($C_1$-$C_6$)alkyl group, an unsubstituted phenyl($C_1$-$C_6$)alkyl group, or a substituted phenyl($C_1$-$C_6$)alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group), X is a halogen atom, and m is an integer of 1 or 2.

9. A fungicide for fruit gardening according to claim 6, 7 or 8, wherein the phenylalanine derivative is an optically active substance.

10. A fungicide for fruit gardening according to claim 6, 7, 8 or 9, wherein the phenylalanine derivative

is a chemically acceptable salt.

11. A fungicide for fruit gardening according to claim 6, 7, 8 or 9, wherein the phenylalanine derivative is a coordination compound.

12. A method for applying a plant disease controller which comprises applying a fungicide for fruit gardening according to any of claims 6 to 11 in an effective dosage for controlling diseases of fruit crops.

AMENDED CLAIMS

[received by the International Bureau on 14 April 1997 (14.04.97); original claims 1 and 2 amended; remaining claims unchanged (6 pages)]

selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; a diphenyl($C_1$-$C_6$)alkyl group; or an aromatic heterocyclic ($C_1$-$C_6$)alkyl group having on the ring one or more heteroatoms which may be the same or different and are selected from the group consisting of oxygen atom, sulfur atom and nitrogen atom, provided that when each of $R^1$ and $R^2$ is a hydrogen atom, $R^{4'}$ is other than hydrogen atom, tert-butyl group and benzyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 2-, 3- or 4-position of the phenyl ring, $R^2$ is other than a methylcarbonyl group, an ethylcarbonyl group and a chloromethylcarbonyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 2-position of the phenyl ring, $R^2$ is other than a trifluoromethylcarbonyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 3-position of the phenyl ring, $R^2$ is other than a phenylcarbonyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 4-position of the phenyl ring, $R^2$ is other than a tert-butoxycarbonyl

group; when $R^1$ is a hydrogen atom, $R^{4'}$ is an ethyl group and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 4-position of the phenyl ring, $R^2$ is other than a phenylmethoxycarbonyl group; and when $R^1$ is a hydrogen atom, $R^{4'}$ is a benzyl group and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 4-position of the phenyl ring, $R^2$ is other than a tert-butoxycarbonyl group), a group represented by the formula:

$$N(R^5)-R^6$$

(wherein $R^5$ is a hydrogen atom; a $(C_1-C_8)$alkyl group; a cyclo$(C_3-C_8)$alkyl group; a $(C_2-C_6)$alkenyl group; a $(C_2-C_6)$alkynyl group; an unsubstituted cyano$(C_1-C_6)$alkyl group; a substituted cyano$(C_1-C_6)$alkyl group having one or more substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, halo$(C_1-C_6)$alkyl groups, $(C_1-C_6)$-alkoxy groups and phenyl group; a $(C_1-C_6)$alkoxy$(C_1-C_6)$-alkoxy$(C_1-C_6)$alkyl group; an unsubstituted amino$(C_1-C_6)$-alkyl group; a substituted amino$(C_1-C_6)$alkyl group having 1 or 2 substituents which may be the same or

be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)-alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylenedioxy groups, phenyl group and phenoxy group; or a guanidyl-($C_1$-$C_6$)alkyl group, and $R^6$ is a hydrogen atom, a ($C_1$-$C_6$)alkyl group or a ($C_2$-$C_6$)alkenyl group, $R^5$ and $R^6$ being able to be taken together to represent a ($C_1$-$C_6$)-alkylene group which may contain an oxygen atom or a nitrogen atom between adjacent carbon atoms of the carbon chain, and said ($C_1$-$C_6$)alkylene group being able to form a ring and have on the ring one or more substituents which may be the same or different and are selected from the group consisting of ($C_1$-$C_6$)alkyl groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, phenyl group, phenyl($C_1$-$C_6$)alkyloxycarbonyl groups and phenyl($C_1$-$C_6$)alkyloxy groups, provided that $R^1$, $R^2$, $R^5$ and $R^6$ are not hydrogen atoms at the same time, and that when $R^1$ is a tert-butoxycarbonyl group and $R^5$ is a benzyl group, $R^6$ is other than methyl group; when each of $R^1$, $R^5$ and $R^6$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 2-, 3- or 4-position of the phenyl ring, $R^2$ is other than an ethyl group; and when each of $R^1$ and $R^6$ is a hydrogen atom, $R^5$ is a benzyl group and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at

4-position of the phenyl ring, $R^2$ is other than an ethylcarbonyl group) or a group represented by the formula:

$$NHCH(R^7)(CH_2)_nCOOR^8$$

(wherein $R^7$ is a hydrogen atom, a $(C_1-C_6)$alkyl group, a cyclo$(C_3-C_8)$alkyl group, a cyclo$(C_3-C_8)$alkyl$(C_1-C_6)$alkyl group, a $(C_1-C_6)$alkoxy$(C_1-C_6)$alkyl group, a hydroxy-

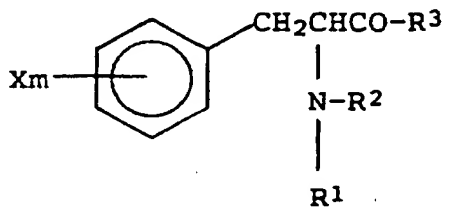
other than hydrogen atom, tert-butyl group and benzyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 2-, 3- or 4-position of the phenyl ring, $R^2$ is other than a methylcarbonyl group, an ethylcarbonyl group and a chloromethylcarbonyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 2-position of the phenyl ring, $R^2$ is other than a trifluoromethylcarbonyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 3-position of the phenyl ring, $R^2$ is other than a phenylcarbonyl group; when each of $R^1$ and $R^{4'}$ is a hydrogen atom and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 4-position of the phenyl ring, $R^2$ is other than a tert-butoxycarbonyl group; when $R^1$ is a hydrogen atom, $R^{4'}$ is an ethyl group and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 4-position of the phenyl ring, $R^2$ is other than a phenylmethoxycarbonyl group; and when $R^1$ is a hydrogen atom, $R^{4'}$ is a benzyl group and a fluorine atom on a phenyl ring of the formula (Ia) is substituted at 4-position of the phenyl ring, $R^2$ is other than a tert-butoxycarbonyl group).

3. A phenylalanine derivative according to claim 1 or 2, which is an optically active substance.

4. A phenylalanine derivative according to claim 1, 2 or 3, which is a chemically acceptable salt.

5. A phenylalanine derivative according to claim 1 or 2, which is a coordination compound.

6. A fungicide for fruit gardening comprising as an active ingredient a phenylalanine derivative represented by the general formula (I):




(I)

wherein $R^1$ is a hydrogen atom or a ($C_1$-$C_8$)alkyl group, $R^2$ is a hydrogen atom; a ($C_1$-$C_8$)alkyl group; a ($C_1$-$C_6$)-alkoxycarbonyl group; an unsubstituted ($C_1$-$C_6$)alkyl-carbonyl group; a substituted ($C_1$-$C_6$)alkylcarbonyl group having as the substituent(s) one or more halogen atoms which may be the same or different; an unsubstituted phenyl($C_1$-$C_6$)alkyl group; a substituted phenyl($C_1$-$C_6$)-alkyl group having on the ring 1 to 5 substituents which may be the same or different and are selected from the group consisting of halogen atoms, nitro group, cyano group, ($C_1$-$C_6$)alkyl groups, halo($C_1$-$C_6$)alkyl groups, ($C_1$-$C_6$)alkoxy groups, halo($C_1$-$C_6$)alkoxy groups, carboxyl group, ($C_1$-$C_6$)alkoxycarbonyl groups, ($C_1$-$C_6$)alkylene-

# INTERNATIONAL SEARCH REPORT

Inte: mal Application No
PCT/JP 96/03484

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C229/36 C07C233/46 C07C237/20 C07C271/22 A01N37/18
A01N37/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 283 956 A (BIO-MEGA ) 28 September 1988<br>see example 1<br>--- | 1-3 |
| X | JOURNAL OF MEDICINAL CHEMISTRY,<br>vol. 32, no. 5, May 1989, WASHINGTON US,<br>pages 1108-1118, XP000611482<br>GEORGE W. HARDY ET AL.: "Peripherally Acting Enkephalin Analogues. 2. Polar Tri- and Tetrapeptides"<br>see page 1111; examples 15U,15V; table IV<br>--- | 1-3 |
| X | US 3 707 559 A (ROBERT H. MAZUR ET AL) 26 December 1972<br>see example 19<br>---<br>-/-- | 1,2 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 25 February 1997 | 06. 03. 97 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+ 31-70) 340-3016 | Zervas, B |

Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Inter ›nal Application No
PCT/JP 96/03484

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | JOURNAL OF PHARMACEUTICAL SCIENCES, vol. 67, no. 4, April 1978, WASHINGTON US, pages 520-526, XP002026113 THEODORE T. OTANI ET AL.: "Effect of Acylated Amino Acids and Acylated Amino Acid Analogs on Microbial Antitumor Screen" see page 521, table I, line 7-9; table II, line 3-5; page 522, table III, line 8-10 --- | 1-3 |
| X | DATABASE CROSSFIRE Beilstein Informationssysteme GmbH, Frankfurt DE XP002026114 see BRN (Beilstein Registry Number)=2885257 & AUST. J. CHEM., vol. 26, 1973, pages 135-138, --- | 1,2 |
| X | DATABASE CROSSFIRE Beilstein Informationssysteme GmbH, Frankfurt DE XP002026115 see BRN=6636870 & RUSS. J. BIOORG. CHEM. (ENGL. TRANSL.), vol. 19, no. 4, 1993, pages 236-240, --- | 1-3 |
| X | DATABASE CROSSFIRE Beilstein Informationssysteme GmbH, Frankfurt DE XP002026116 see BRN=5381672 & TETRAHEDRON: ASYMMETRIE, vol. 3, no. 4, 1992, pages 555-566, --- | 1-3 |
| X | DATABASE CROSSFIRE Beilstein Informationssysteme GmbH, Frankfurt DE XP002026117 see BRN=3959735 & AUST. J. CHEM., vol. 31, 1978, page 2187-2189 --- -/-- | 1,2 |

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# INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 96/03484

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | DATABASE CROSSFIRE<br>Beilstein Informationssysteme GmbH,<br>Frankfurt DE<br>XP002026118<br>see BRN=3010470<br>& HELV. CHIM. ACTA,<br>vol. 56, no. 6, 1973,<br>pages 1838-1845,<br>--- | 1,2 |
| X | DATABASE CROSSFIRE<br>Beilstein Informationssysteme GmbH,<br>Frankfurt DE<br>XP002026119<br>see BRN=4564447<br>& J. ORG. CHEM. ,<br>vol. 57, no. 12, 1992,<br>pages 3397-3404,<br>--- | 1-3 |
| X | DATABASE WPI<br>Section Ch, Week 7520<br>Derwent Publications Ltd., London, GB;<br>Class C03, AN 75-33116W<br>XP002026120<br>& JP 49 109 536 A (MEIJI CONF) , 18<br>October 1974<br>cited in the application<br>see abstract<br>----- | 6-12 |

1

# INTERNATIONAL SEARCH REPORT

Ir ational application No.
PCT/JP 96/ 03484

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see attached sheet

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/210

The definition of the substituents in the claims 1 to 12 is too general and encompasses too broad a range of possible combinations of different chemical groups, only partly supported by the examples given in the descriptive part of the application. Since many compounds, which are disclosed in claim 1, are already described in the prior art *) the search has been based on the examples (cf Art. 6 PCT) and claims 1 to 12 have been searched incompletely.

*): See the large number of X-documents, which can be cited even for an incomplete searched claim 1; a further search would led to a large number of additional X-documents.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter ...nal Application No
PCT/JP 96/03484

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 283956 A | 28-09-88 | AU 605259 B | 10-01-91 |
| | | AU 1316788 A | 24-11-88 |
| | | DE 3875765 A | 17-12-92 |
| | | JP 1006296 A | 10-01-89 |
| | | US 5095004 A | 10-03-92 |
| | | US 5376635 A | 27-12-94 |
| US 3707559 A | 26-12-72 | NONE | |